```
=> d his full

     (FILE 'HOME' ENTERED AT 08:11:55 ON 27 JUN 2005)
               DEL GITLIPR/A

     FILE 'REGISTRY' ENTERED AT 08:12:51 ON 27 JUN 2005
L1                STR
L2                STR L1
L3             12 SEA SSS SAM L2
                  DEL QAZ122F0/A
L4            224 SEA SSS FUL L2
                  SAV TEM QAZ122C1/A L4
L5                STR L2
L6              0 SEA SUB=L4 SSS SAM L5
L7             13 SEA SUB=L4 SSS FUL L5
                  ACT QAZ122C12PR/A
                 ---------
L8                STR
L9   (      13409)SEA CSS FUL L8
L10               STR
L11            20 SEA SUB=L9 SSS FUL L10
                  ---------
L12               STR L5
L13             1 SEA SUB=L4 SSS SAM L12
                  D SCA
L14            19 SEA SUB=L4 SSS FUL L12
                  SAV TEM QAZIC12R/A L14

     FILE 'HCAPLUS' ENTERED AT 08:22:00 ON 27 JUN 2005
L15            12 SEA ABB=ON  PLU=ON  L7
L16             1 SEA ABB=ON  PLU=ON  L14 AND L11
                  E VAN RHEENEN V/AU
L17            31 SEA ABB=ON  PLU=ON  ("VAN RHEENEN V"/AU OR "VAN RHEENEN
                  VERLAN"/AU OR "VAN RHEENEN VERLAN H"/AU OR "VAN RHEENEN VERLAN
                  HENRY"/AU OR "VAN RHEENEN VERLAND HENRY"/AU)
                  E HESSLER E/AU
L18            22 SEA ABB=ON  PLU=ON  ("HESSLER ED"/AU OR "HESSLER ED J"/AU OR
                  "HESSLER EDWARD"/AU OR "HESSLER EDWARD J"/AU OR "HESSLER
                  EDWARD JAMES"/AU)
L19             2 SEA ABB=ON  PLU=ON  (BRID? (1A)ORG?)/CS,PA

     FILE 'HCAOLD' ENTERED AT 08:23:44 ON 27 JUN 2005
L20             3 SEA ABB=ON  PLU=ON  L7
                  SEL AN
                  EDIT E1-E3 /AN /OREF

     FILE 'HCAPLUS' ENTERED AT 08:24:11 ON 27 JUN 2005
L21             6 SEA ABB=ON  PLU=ON  ("CA59:8825E"/OREF OR "CA62:621C"/OREF OR
                  "CA63:655G"/OREF)
L22             1 SEA ABB=ON  PLU=ON  (L15 OR L21) AND (L17 OR L18 OR L19)
L23            15 SEA ABB=ON  PLU=ON  (L15 OR L21) NOT L22
L24               QUE ABB=ON  PLU=ON  PY<+2001 OR AY<=2001 OR PRY<=2001 OR
                  PD<20010608 OR AD<20010608 OR PRD<20010608
L25            15 SEA ABB=ON  PLU=ON  L23 AND L24
L26             1 SEA ABB=ON  PLU=ON  L16 AND (L17 OR L18 OR L19)
L27             1 SEA ABB=ON  PLU=ON  L22 OR L26

     FILE 'HCAOLD' ENTERED AT 08:27:47 ON 27 JUN 2005
               SEL HIT RN L20

     FILE 'REGISTRY' ENTERED AT 08:27:56 ON 27 JUN 2005
L28             4 SEA ABB=ON  PLU=ON  (102490-33-5/RN OR 1624-60-8/RN OR
                  1103-94-2/RN OR 1249-41-8/RN)

=> b reg
FILE 'REGISTRY' ENTERED AT 08:28:18 ON 27 JUN 2005
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Property values tagged with IC are from the ZIC/VINITI data file provided by InfoChem.

STRUCTURE FILE UPDATES: 26 JUN 2005 HIGHEST RN 852987-17-8
DICTIONARY FILE UPDATES: 26 JUN 2005 HIGHEST RN 852987-17-8

New CAS Information Use Policies, enter HELP USAGETERMS for details.

TSCA INFORMATION NOW CURRENT THROUGH JANUARY 18, 2005

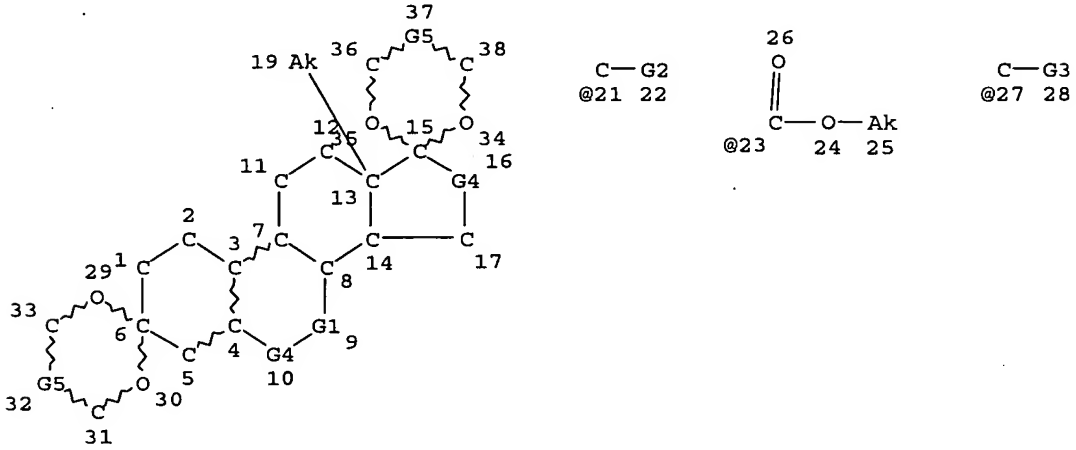
Please note that search-term pricing does apply when conducting SmartSELECT searches.

****
* *
* The CA roles and document type information have been removed from *
* the IDE default display format and the ED field has been added, *
* effective March 20, 2005. A new display format, IDERL, is now *
* available and contains the CA role and document type information. *
* *
****

Crossover limits have been increased. See HELP CROSSOVER for details.

Experimental and calculated property data are now available. For more information enter HELP PROP at an arrow prompt in the file or refer to the file summary sheet on the web at:
http://www.cas.org/ONLINE/DBSS/registryss.html

=> d que sta l7
L2 STR

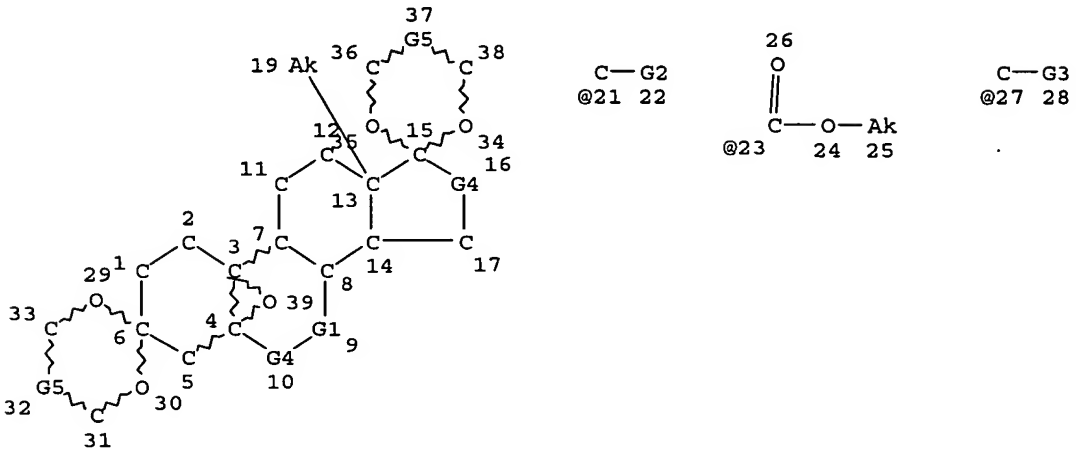


VAR G1=C/21
VAR G2=AK/23
VAR G3=AK/OH/X
VAR G4=C/27
REP G5=(0-1) C
NODE ATTRIBUTES:
DEFAULT MLEVEL IS ATOM
DEFAULT ECLEVEL IS LIMITED

GRAPH ATTRIBUTES:
RING(S) ARE ISOLATED OR EMBEDDED

NUMBER OF NODES IS 36

STEREO ATTRIBUTES: NONE
L4 224 SEA FILE=REGISTRY SSS FUL L2
L5 STR



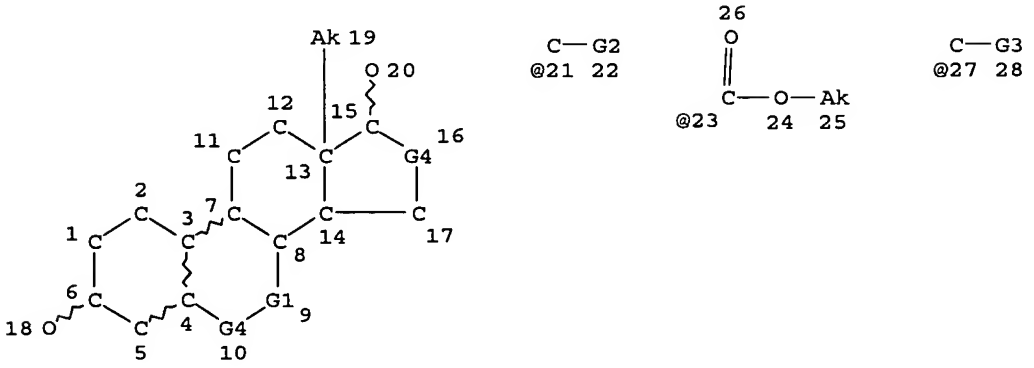
VAR G1=C/21
VAR G2=AK/23
VAR G3=AK/OH/X
VAR G4=C/27
REP G5=(0-1) C
NODE ATTRIBUTES:
DEFAULT MLEVEL IS ATOM
DEFAULT ECLEVEL IS LIMITED

GRAPH ATTRIBUTES:
RING(S) ARE ISOLATED OR EMBEDDED
NUMBER OF NODES IS 37

STEREO ATTRIBUTES: NONE
L7 13 SEA FILE=REGISTRY SUB=L4 SSS FUL L5

100.0% PROCESSED 37 ITERATIONS 13 ANSWERS
SEARCH TIME: 00.00.01

=> d que sta l11
L8 STR



VAR G1=C/21
VAR G2=AK/23

VAR G3=AK/OH/X
VAR G4=C/27
NODE ATTRIBUTES:
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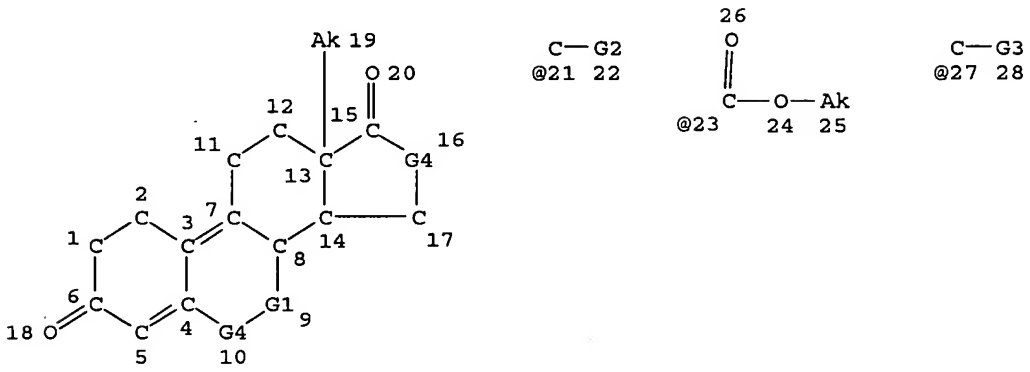
CONNECT IS M1 RC AT 4
CONNECT IS M1 RC AT 6
CONNECT IS M1 RC AT 15
CONNECT IS M1 RC AT 18
CONNECT IS M1 RC AT 20
DEFAULT MLEVEL IS ATOM
DEFAULT ECLEVEL IS LIMITED

GRAPH ATTRIBUTES:
RING(S) ARE ISOLATED OR EMBEDDED
NUMBER OF NODES IS 28

STEREO ATTRIBUTES: NONE
L9 (13409)SEA FILE=REGISTRY CSS FUL L8
L10 STR



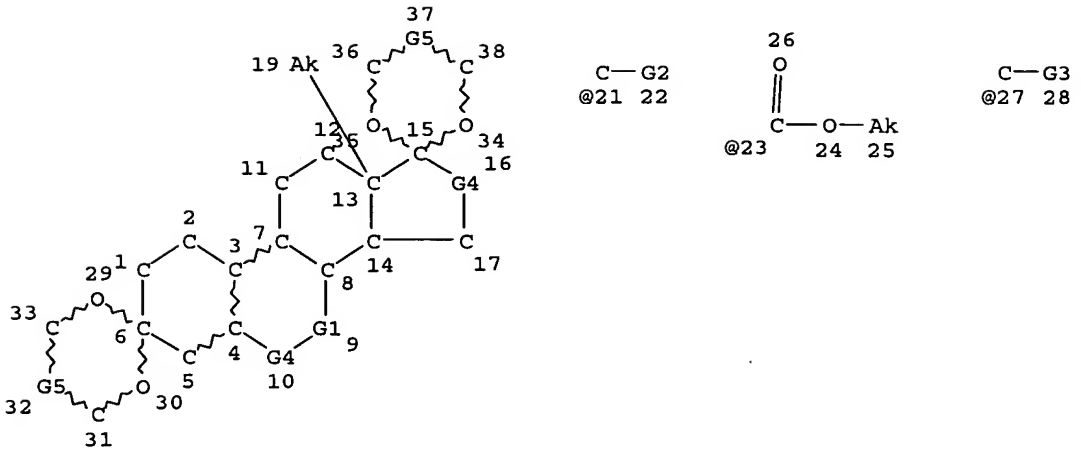
VAR G1=C/21
VAR G2=AK/23
VAR G3=AK/OH/X
VAR G4=C/27
NODE ATTRIBUTES:
DEFAULT MLEVEL IS ATOM
DEFAULT ECLEVEL IS LIMITED

GRAPH ATTRIBUTES:
RING(S) ARE ISOLATED OR EMBEDDED
NUMBER OF NODES IS 28

STEREO ATTRIBUTES: NONE
L11 20 SEA FILE=REGISTRY SUB=L9 SSS FUL L10

100.0% PROCESSED 24 ITERATIONS 20 ANSWERS
SEARCH TIME: 00.00.01

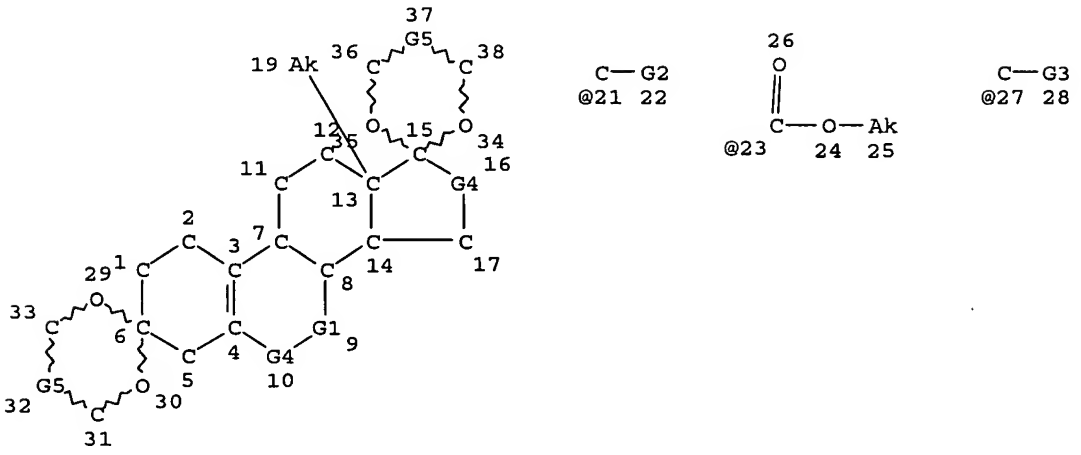
=> d que sta l14
L2 STR



VAR G1=C/21
VAR G2=AK/23
VAR G3=AK/OH/X
VAR G4=C/27
REP G5=(0-1) C
NODE ATTRIBUTES:
DEFAULT MLEVEL IS ATOM
DEFAULT ECLEVEL IS LIMITED

GRAPH ATTRIBUTES:
RING(S) ARE ISOLATED OR EMBEDDED
NUMBER OF NODES IS 36

STEREO ATTRIBUTES: NONE
L4 224 SEA FILE=REGISTRY SSS FUL L2
L12 STR



VAR G1=C/21
VAR G2=AK/23
VAR G3=AK/OH/X
VAR G4=C/27
REP G5=(0-1) C
NODE ATTRIBUTES:
DEFAULT MLEVEL IS ATOM
DEFAULT ECLEVEL IS LIMITED

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GRAPH ATTRIBUTES:
RING(S) ARE ISOLATED OR EMBEDDED
NUMBER OF NODES IS  36

STEREO ATTRIBUTES: NONE
L14          19 SEA FILE=REGISTRY SUB=L4 SSS FUL L12

100.0% PROCESSED      52 ITERATIONS  (     1 INCOMPLETE)      19 ANSWERS
SEARCH TIME: 00.00.01


=> b hcap
FILE 'HCAPLUS' ENTERED AT 08:28:32 ON 27 JUN 2005
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FILE COVERS 1907 - 27 Jun 2005  VOL 143 ISS 1
FILE LAST UPDATED: 26 Jun 2005  (20050626/ED)

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 This file contains CAS Registry Numbers for easy and accurate
 substance identification.

=> d all fhitstr l27 tot

L27  ANSWER 1 OF 1  HCAPLUS  COPYRIGHT 2005 ACS on STN
AN   2002:964483  HCAPLUS
DN   138:24878
ED   Entered STN:  20 Dec 2002
TI   Process for preparing estra-4,9(10)-diene-3,17-dione steroids from
     19-nor-androst-4-ene-3-one steroids
IN   Van Rheenen, Verlan H.; Hessler, Edward J.
PA   Bridge Organics Co., USA
SO   PCT Int. Appl., 23 pp.
     CODEN: PIXXD2
DT   Patent
LA   English
IC   ICM  C12N
CC   32-3 (Steroids)
FAN.CNT 1
     PATENT NO.          KIND   DATE        APPLICATION NO.        DATE
     --------------      ----   --------    --------------------   --------
PI   WO 2002101014        A2    20021219    WO 2002-US18305        20020607
     WO 2002101014        A3    20040325
     WO 2002101014        B1    20040506
         W:  AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN,
             CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH,
             GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR,
             LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, OM, PH,
             PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TN, TR, TT, TZ,
             UA, UG, UZ, VN, YU, ZA, ZM, ZW
         RW: GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW, AM, AZ, BY,
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KG, KZ, MD, RU, TJ, TM, AT, BE, CH, CY, DE, DK, ES, FI, FR, GB,
GR, IE, IT, LU, MC, NL, PT, SE, TR, BF, BJ, CF, CG, CI, CM, GA,
GN, GQ, GW, ML, MR, NE, SN, TD, TG

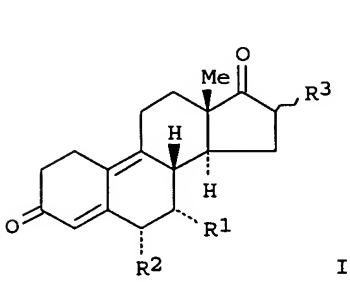
	US 2003004333	A1	20030102	US 2002-163727	20020606
	US 6812358	B2	20041102		
	US 2004087785	A1	20040506	US 2003-695122	20031028
PRAI	US 2001-296999P	P	20010608		
	US 2002-163727	A	20020606		

CLASS

PATENT NO.	CLASS	PATENT FAMILY CLASSIFICATION CODES
WO 2002101014	ICM	C12N
WO 2002101014	ECLA	C07J001/00C2; C07J071/00B1
US 2003004333	NCL	552/623.000; 540/543.000
	ECLA	C07J001/00C2; C07J071/00B1
US 2004087785	NCL	540/008.000; 540/076.000
	ECLA	C07J001/00C2; C07J071/00B1

OS CASREACT 138:24878; MARPAT 138:24878

GI



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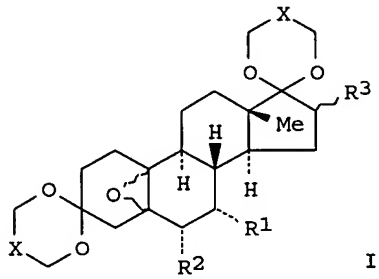


II

AB The present invention discloses a novel process for preparing estra-4,9(10)-diene-3,17-dione derivs. such as I [R1 = Me, H, CO2Me; R2 = Me, F, H; R3 = Me, OH, F, H], from readily available 19-nor-androst-4-ene-3-one derivs. such as II [X = bond, C(Me)2, CH2], by a three-step process. Thus, epoxidn. of 7α-methyl-estra-5(10)-ene-3,17-dione-3,17-bis-ethylene glycol ketal afforded 7α-methyl-estra-5(10)-oxido-3,17-dione-3,17-bis-ethylene glycol ketal which upon treatment with hydrochloric acid provided 10-hydroxy-7α-methyl-estra-4-ene-3,17-dione (III) and 5,10-dihydroxy-7α-methyl-estra-4-ene-3,17-dione (IV). III and IV were reacted with concentrated sulfuric acid to afford estra-4,9(10)-diene-3,17-dione I [R1 = Me; R2, R3 = H]. Products of this process are important intermediates in the preparation of biol. active substances.

ST estradienedione steroid prepn norandrosteneone epoxidn; oxidoestradione dihydroxyestraenedione hydroxyestraenedione prepn

IT Ketals
RL: RCT (Reactant); RACT (Reactant or reagent)
(estra-5(10)-ene-3,17-dione-3,17-bis-ketal derivative; in preparation of estra-4,9(10)-diene steroid derivs.)

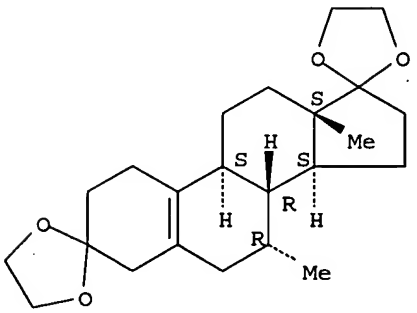
IT Acids, reactions
RL: RGT (Reagent); RACT (Reactant or reagent)
(inorg.; in preparation of estra-4,9(10)-diene steroids from 10-hydroxy-estra-4-ene-3,17-dione and 5,10-dihydroxy-estra-4-ene-3,17-dione steroids)

IT Epoxidation
(of estra-5(10)-ene-3,17-dione-3,17-bis-glycol ketal in preparation of estra-5(10)-oxido-3,17-dione-3,17-bis-glycol ketal)

IT Estrogens
RL: IMF (Industrial manufacture); SPN (Synthetic preparation); PREP (Preparation)
(preparation of estra-4,9(10)-diene steroids from 19-nor-androst-4-ene-3-one

steroids)
IT 19-Norsteroids
RL: RCT (Reactant); RACT (Reactant or reagent)
(preparation of estra-4,9(10)-diene steroids from 19-nor-androst-4-ene-3-one steroids)
IT 13209-45-5P, Estra-4,6-diene-3,17-dione **478156-84-2P**
478156-85-3P 478156-86-4P 478156-87-5P 478156-88-6P
478156-89-7P 478156-91-1P **478156-93-3P** 478156-94-4P
478156-96-6P 478242-79-4P
RL: IMF (Industrial manufacture); RCT (Reactant); SPN (Synthetic preparation); PREP (Preparation); RACT (Reactant or reagent)
(preparation of estra-4,9(10)-diene steroids from 19-nor-androst-4-ene-3-one steroids)
IT **5173-46-6P**, Estra-4,9-diene-3,17-dione **24130-12-9P**
30164-84-2P 478156-90-0P 478156-92-2P
478156-97-7P
RL: IMF (Industrial manufacture); SPN (Synthetic preparation); PREP (Preparation)
(preparation of estra-4,9(10)-diene steroids from 19-nor-androst-4-ene-3-one steroids)
IT 734-32-7, 19-Nor-androst-4-ene-3,17-dione **2220-74-8** 2503-06-2,
Estra-5(10),9(11)-diene-3,17-dione 17000-78-1 33585-96-5
139444-50-1 478156-95-5
RL: RCT (Reactant); RACT (Reactant or reagent)
(preparation of estra-4,9(10)-diene steroids from 19-nor-androst-4-ene-3-one steroids)
IT 79-21-0, Peracetic acid 937-14-4, m-Chloroperbenzoic acid 7664-38-2, Phosphoric acid, reactions 7664-93-9, Sulfuric acid, reactions
RL: RGT (Reagent); RACT (Reactant or reagent)
(preparation of estra-4,9(10)-diene steroids from 19-nor-androst-4-ene-3-one steroids)
IT **478156-84-2P**
RL: IMF (Industrial manufacture); RCT (Reactant); SPN (Synthetic preparation); PREP (Preparation); RACT (Reactant or reagent)
(preparation of estra-4,9(10)-diene steroids from 19-nor-androst-4-ene-3-one steroids)
RN 478156-84-2 HCAPLUS
CN Estr-5(10)-ene-3,17-dione, 7-methyl-, cyclic bis(1,2-ethanediyl acetal), (7α)- (9CI) (CA INDEX NAME)

Absolute stereochemistry.



=> d all hitstr l25 tot

L25 ANSWER 1 OF 15 HCAPLUS COPYRIGHT 2005 ACS on STN
AN 1996:31798 HCAPLUS
DN 124:87466
ED Entered STN: 17 Jan 1996
TI Structure-Activity Relationships of a New Family of Steroidal Aromatase Inhibitors. 1. Synthesis and Evaluation of a Series of Analogs Related to

19-[(Methylthio)methyl]androstenedione (RU54115)

AU Lesuisse, Dominique; Gourvest, Jean-Francois; Benslimane, Ouafae; Canu, Frank; Delaisi, Christine; Doucet, Bernard; Hartmann, Catherine; Lefrancois, Jean-Michel; Tric, Bernadette; et al.
CS Centre de Recherche, Roussel Uclaf, Romainville, 93230, Fr.

SO Journal of Medicinal Chemistry (1996), 39(3), 757-72
CODEN: JMCMAR; ISSN: 0022-2623
PB American Chemical Society
DT Journal
LA English
CC 32-4 (Steroids)
Section cross-reference(s): 1, 7

AB During the course of a study aimed at the search for new potent aromatase inhibitors, several new androstenedione analogs were synthesized and evaluated. This study led to the discovery of 19-[(methylthio)methyl]androsta-4,9(11)-diene-3,17-dione (RU54115). The object of the present series of papers is to disclose the result of the structure-activity relationship studies that gave rise to this compound This first part deals mainly with the substitution in the 19-position of the steroid nucleus. Several parameters were varied, the length of the chain and its rigidity and branching, as well as the nature of the heteroatom itself and its substitution. The interaction of these new compds. with human placental aromatase in competition with the substrate androstenedione was studied by difference visible spectroscopy. The in vivo aromatase-inhibiting activities were evaluated by measuring the estradiol lowering after oral administration of the compds. to PMSG-primed female rats.

ST steroidal aromatase inhibitor methylthiomethylandrostenedione structure activity; androstenedione methylthiomethyl steroidal aromatase inhibitor

IT Molecular structure-biological activity relationship
(testosterone A-ring reductase-inhibiting, synthesis steroidal aromatase inhibitor structure-activity relationships of 19-[(methylthio)methyl]androstenedione analogs)

IT 137437-39-9P
RL: BAC (Biological activity or effector, except adverse); BSU (Biological study, unclassified); RCT (Reactant); SPN (Synthetic preparation); BIOL (Biological study); PREP (Preparation); RACT (Reactant or reagent)
(synthesis steroidal aromatase inhibitor structure-activity relationships of 19-[(methylthio)methyl]androstenedione analogs)

IT 137437-16-2P 137437-17-3P 137437-20-8P 137437-26-4P 137437-32-2P
137437-33-3P 137437-36-6P 137437-37-7P 137437-40-2P 137437-43-5P
137437-45-7P 137437-46-8P 137437-47-9P 137437-48-0P 137437-50-4P
137437-52-6P 137437-54-8P 137437-64-0P 172427-87-1P 172427-90-6P
172427-91-7P 172427-92-8P 172427-93-9P 172427-98-4P 172428-00-1P
172428-02-3P 172428-04-5P
RL: BAC (Biological activity or effector, except adverse); BSU (Biological study, unclassified); SPN (Synthetic preparation); BIOL (Biological study); PREP (Preparation)
(synthesis steroidal aromatase inhibitor structure-activity relationships of 19-[(methylthio)methyl]androstenedione analogs)

IT 9039-48-9, Aromatase
RL: BPR (Biological process); BSU (Biological study, unclassified); BIOL (Biological study); PROC (Process)
(synthesis steroidal aromatase inhibitor structure-activity relationships of 19-[(methylthio)methyl]androstenedione analogs)

IT 528-76-7, 2,4-Dinitrobenzenesulfenyl chloride 1066-54-2, (Trimethylsilyl)acetylene 4333-56-6, Bromocyclopropane 55180-24-0
102490-33-5 135215-65-5 135215-66-6 135215-67-7
172427-99-5 172428-25-0 172585-98-7
RL: RCT (Reactant); RACT (Reactant or reagent)
(synthesis steroidal aromatase inhibitor structure-activity relationships of 19-[(methylthio)methyl]androstenedione analogs)

IT 137437-13-9P 137437-14-0P 137437-15-1P 137437-18-4P 137437-21-9P
137437-22-0P 137437-24-2P 137437-25-3P 137437-31-1P 137437-35-5P
172427-88-2P 172427-89-3P 172427-94-0P 172427-96-2P 172427-97-3P
172428-03-4P 172428-05-6P 172428-06-7P 172428-07-8P 172428-08-9P

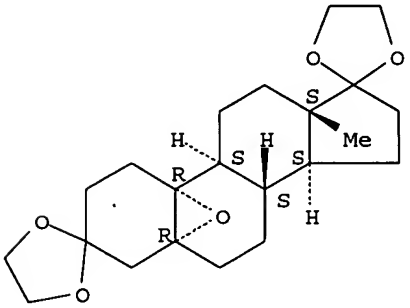
172428-09-0P 172428-10-3P 172428-11-4P 172428-12-5P 172428-13-6P
172428-14-7P 172428-15-8P 172428-16-9P 172428-17-0P 172428-18-1P
172428-19-2P 172428-20-5P 172428-21-6P 172428-22-7P 172428-23-8P
172428-24-9P
RL: RCT (Reactant); SPN (Synthetic preparation); PREP (Preparation); RACT (Reactant or reagent)
(synthesis steroidal aromatase inhibitor structure-activity relationships of 19-[(methylthio)methyl]androstenedione analogs)

IT 99957-76-3P 172427-95-1P 172428-01-2P
RL: SPN (Synthetic preparation); PREP (Preparation)
(synthesis steroidal aromatase inhibitor structure-activity relationships of 19-[(methylthio)methyl]androstenedione analogs)

IT 102490-33-5
RL: RCT (Reactant); RACT (Reactant or reagent)
(synthesis steroidal aromatase inhibitor structure-activity relationships of 19-[(methylthio)methyl]androstenedione analogs)

RN 102490-33-5 HCAPLUS
CN Estrane-3,17-dione, 5,10-epoxy-, cyclic bis(1,2-ethanediyl acetal), (5α,10α)- (9CI) (CA INDEX NAME)

Absolute stereochemistry.



L25 ANSWER 2 OF 15 HCAPLUS COPYRIGHT 2005 ACS on STN
AN 1992:129377 HCAPLUS
DN 116:129377
ED Entered STN: 03 Apr 1992
TI Process for the preparation of 10-(2-propynyl)estr-4-ene-3,17-dione
IN Whitten, Jeffrey P.; Benson, Harvey D.; Rand, Cynthia L.
PA Merrell Dow Pharmaceuticals, Inc., USA
SO Eur. Pat. Appl., 13 pp.
CODEN: EPXXDW
DT Patent
LA English
IC ICM C07J001-00
ICA C07J021-00; C07J071-00; C07J051-00
CC 32-3 (Steroids)
FAN.CNT 1

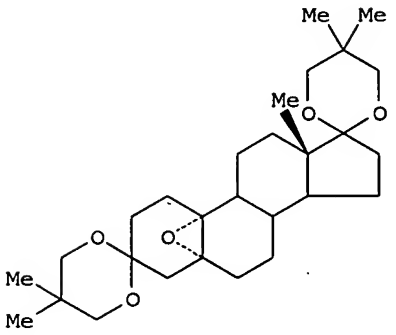
	PATENT NO.	KIND	DATE	APPLICATION NO.	DATE	
PI	EP 459381	A2	19911204	EP 1991-108664	19910528	<--
	EP 459381	A3	19920610			
	EP 459381	B1	19970319			
	R: AT, BE, CH, DE, DK, ES, FR, GB, GR, IT, LI, LU, NL, SE					
	CA 2043280	AA	19911201	CA 1991-2043280	19910524	<--
	AU 9177290	A1	19911205	AU 1991-77290	19910524	<--
	AU 649251	B2	19940519			
	ZA 9103963	A	19920429	ZA 1991-3963	19910524	<--
	AT 150465	E	19970415	AT 1991-108664	19910528	<--
	ES 2101702	T3	19970716	ES 1991-108664	19910528	<--
	HU 57791	A2	19911230	HU 1991-1800	19910529	<--
	HU 212575	B	19960829			

	JP 04235997	A2	19920825	JP 1991-153686	19910530 <--
	JP 2989935	B2	19991213		
	IL 98384	A1	19950330	IL 1991-98384	19910605 <--
	US 5516922	A	19960514	US 1995-468886	19950606 <--
PRAI	US 1990-530674	A	19900530 <--		
	US 1991-692321	A	19910502 <--		
	US 1992-987985	B1	19921209 <--		
	US 1993-114802	B1	19930831 <--		
	US 1994-359708	B1	19941220 <--		

CLASS

PATENT NO.	CLASS	PATENT FAMILY CLASSIFICATION CODES
EP 459381	ICM	C07J001-00
	ICA	C07J021-00; C07J071-00; C07J051-00
EP 459381	ECLA	C07J001/00C2; C07J021/00C2; C07J051/00; C07J071/00B1<--
US 5516922	NCL	552/632.000; 552/630.000 <--

GI



III

AB 10-(2-Propynyl)estr-4-ene-3,17-dione (I) was prepared from 19-norandrost-5(10)-ene-3,17-dione (II) in 5 steps via cuprate addition of Me3SiC.tplbond.CMe. Thus, II was ketalized with Me2C(CH2OH)2, the ketal was treated with N-bromosuccinimide-MgO, followed by dehydrobromination to give the epoxide III. III was treated with the cuprate prepared from Me3SiC.tplbond.CMe, BuLi, and Li methyl-2-thienylcuprate, followed by desilylation and ketal hydrolysis to give I.

ST cuprate addn epoxyandrostane; propynylestrenedione; norandrostenedione propynylation

IT 6224-91-5, 1-Trimethylsilylpropyne
RL: RCT (Reactant); RACT (Reactant or reagent)
(cuprate addition reaction of, with epoxyandrostane)

IT 3962-66-1, Estr-5(10)-ene-3,17-dione
RL: RCT (Reactant); RACT (Reactant or reagent)
(ketalization of)

IT 139444-50-1P
RL: RCT (Reactant); SPN (Synthetic preparation); PREP (Preparation); RACT (Reactant or reagent)
(preparation and bromination-hydroxylation of)

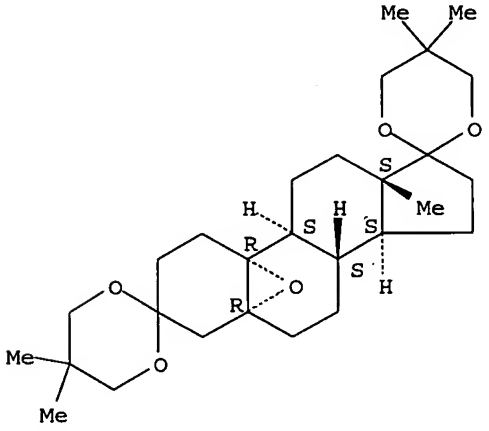
IT 104000-05-7P
RL: RCT (Reactant); SPN (Synthetic preparation); PREP (Preparation); RACT (Reactant or reagent)
(preparation and cuprate addition reaction of)

IT 139444-52-3P
RL: RCT (Reactant); SPN (Synthetic preparation); PREP (Preparation); RACT (Reactant or reagent)
(preparation and deblocking of)

IT 139444-51-2P
RL: RCT (Reactant); SPN (Synthetic preparation); PREP (Preparation); RACT (Reactant or reagent)
(preparation and dehydrobromination of)

IT 117626-56-9P
RL: RCT (Reactant); SPN (Synthetic preparation); PREP (Preparation); RACT (Reactant or reagent)
(preparation and desilylation of)
IT 77016-85-4P
RL: SPN (Synthetic preparation); PREP (Preparation)
(preparation of)
IT 139431-51-9 139522-17-1
RL: RCT (Reactant); RACT (Reactant or reagent)
(propynylation by, of epoxyandrostane)
IT 104000-05-7P
RL: RCT (Reactant); SPN (Synthetic preparation); PREP (Preparation); RACT (Reactant or reagent)
(preparation and cuprate addition reaction of)
RN 104000-05-7 HCAPLUS
CN Estrane-3,17-dione, 5,10-epoxy-, cyclic bis(2,2-dimethyl-1,3-propanediyl acetal), (5α,10α)- (9CI) (CA INDEX NAME)

Absolute stereochemistry.



L25 ANSWER 3 OF 15 HCAPLUS COPYRIGHT 2005 ACS on STN
AN 1989:95624 HCAPLUS
DN 110:95624
ED Entered STN: 17 Mar 1989
TI Preparation of novel 11-arylestrane and 11-arylpregnane derivatives as antiprogestins with low or no antiglucocorticoid activity
IN Groen, Marinus Bernard; De Jongh, Hendrik Paul
PA AKZO N. V., Neth.
SO Eur. Pat. Appl., 11 pp.
CODEN: EPXXDW
DT Patent
LA English
IC ICM C07J041-00
ICS A61K031-565; A61K031-585
CC 32-3 (Steroids)
Section cross-reference(s): 1
FAN.CNT 1

	PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
PI	EP 289073	A1	19881102	EP 1988-200689	19880412 <--
	EP 289073	B1	19911127		
	R: AT, BE, CH, DE, ES, FR, GB, GR, IT, LI, NL, SE				
	AT 69820	E	19911215	AT 1988-200689	19880412 <--
	ES 2045082	T3	19940116	ES 1988-200689	19880412 <--
	ZA 8802643	A	19881130	ZA 1988-2643	19880414 <--
	FI 8801826	A	19881025	FI 1988-1826	19880419 <--

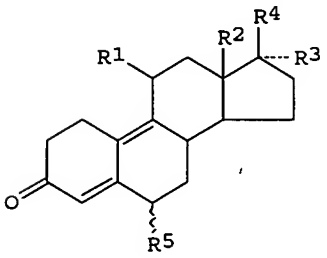
	FI 88396	B	19930129			
	FI 88396	C	19930510			
	US 4871724	A	19891003	US 1988-183851	19880420	<--
	CA 1297472	A1	19920317	CA 1988-564606	19880420	<--
	DK 8802218	A	19881025	DK 1988-2218	19880422	<--
	DK 168294	B1	19940307			
	AU 8815072	A1	19881027	AU 1988-15072	19880422	<--
	AU 608831	B2	19910418			
	JP 63280097	A2	19881117	JP 1988-100010	19880422	<--
	CN 88102416	A	19881214	CN 1988-102416	19880423	<--
	CN 1019978	B	19930303			
	KR 9705318	B1	19970415	KR 1988-4653	19880423	<--
PRAI	NL 1987-970	A	19870424	<--		
	EP 1988-200689	A	19880412	<--		

CLASS

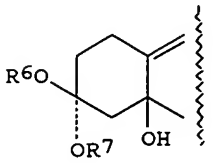
PATENT NO.	CLASS	PATENT FAMILY CLASSIFICATION CODES
EP 289073	ICM	C07J041-00
	ICS	A61K031-565; A61K031-585
US 4871724	NCL	514/173.000; 514/175.000; 514/181.000; 540/017.000; 540/023.000; 552/594.000; 552/597.000; 552/602.000; 552/605.000; 552/612.000; 552/621.000; 552/644.000; 552/647.000 <--

OS MARPAT 110:95624

GI



I



II

AB The title compds. [I; R1 = aminoaryl; R2 = C1-4 alkyl; R3 = H, OH, substituted (unsatd.) C1-8 hydrocarbyl; R4 = OH, acyloxy, substituted acyl; R3R4 = atoms to complete a ring; R5 = C1-4 hydrocarbyl] useful as antiprogestins (no data) were prepared 5α,6α-Epoxy-11β-hydroxyestrane-3,17-dione-3,17-diethylene acetal (preparation given) was treated with MeMgCl in PhMe/THF and the product was dehydrated with POCl3/pyridine to give 6-β-methylestra-5(10),9(11)-diene-3,17-dione-3,17-diethylene acetal. The latter was converted in several steps to 11β-[4-(dimethylamino)phenyl]-17β-hydroxy-17α-(3-hydroxy-1-propynyl)-6β-methylestra-4,9-diene-3-one.

ST estradienone pregnadienone prepn antiprogestin

IT Progestogens
RL: RCT (Reactant); RACT (Reactant or reagent)
(antagonists, arylestrane and arylpregnane derivs. as)

IT Contraceptives
(arylestrane and arylpregnane derivs.)

IT 676-58-4
RL: RCT (Reactant); RACT (Reactant or reagent)
(Grignard reaction of, with epoxy hydroxyestranedione derivative)

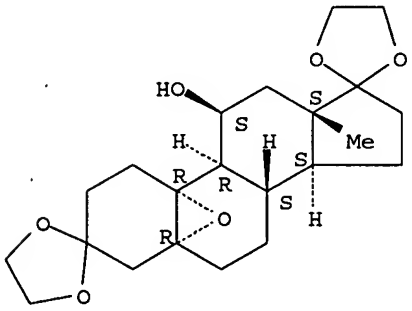
IT 118968-39-1
RL: RCT (Reactant); RACT (Reactant or reagent)
(cyclization of, in preparation of antiprogestin)

IT 118968-57-3
RL: RCT (Reactant); RACT (Reactant or reagent)
(dehydration/deketalization of, in preparation of antiprogestin)

IT 59017-03-7

RL: RCT (Reactant); RACT (Reactant or reagent)
(epoxidn. of, in preparation of antiprogestin)
IT 6089-04-9, Propargyl alcohol tetrahydropyranyl ether
RL: RCT (Reactant); RACT (Reactant or reagent)
(metalation and condensation of, with estradienedione derivative)
IT 118968-55-1
RL: RCT (Reactant); RACT (Reactant or reagent)
(oxidation of)
IT 118968-37-9P 118968-38-0P 118968-39-1P 118968-40-4P 118968-41-5P
118968-42-6P
RL: SPN (Synthetic preparation); PREP (Preparation)
(preparation of, as antiprogestin)
IT 118968-54-0P 118968-56-2P 118968-58-4P
RL: SPN (Synthetic preparation); PREP (Preparation)
(preparation of, as intermediate for antiprogestin)
IT 118968-43-7P **118968-44-8P** 118968-45-9P 118968-46-0P
118968-47-1P 118968-48-2P 118968-49-3P 118968-50-6P 118968-51-7P
118968-52-8P 118968-53-9P
RL: SPN (Synthetic preparation); PREP (Preparation)
(preparation of, as intermediate of antiprogestin)
IT 119066-24-9P
RL: SPN (Synthetic preparation); PREP (Preparation)
(preparation of, as progestin intermediate)
IT **118968-44-8P**
RL: SPN (Synthetic preparation); PREP (Preparation)
(preparation of, as intermediate of antiprogestin)
RN 118968-44-8 HCAPLUS
CN Estrane-3,17-dione, 5,10-epoxy-11-hydroxy-, cyclic bis(1,2-ethanediyl acetal), (5α,10α,11β)- (9CI) (CA INDEX NAME)

Absolute stereochemistry.



L25 ANSWER 4 OF 15 HCAPLUS COPYRIGHT 2005 ACS on STN
AN 1989:71676 HCAPLUS
DN 110:71676
ED Entered STN: 04 Mar 1989
TI [19-14C]Androstenedione: a new substrate for assaying aromatase and studying its reaction mechanism
AU Covey, Douglas F.; McMullan, Patrick C.; Wixler, Linda L.; Cabell, Mayo
CS Sch. Med., Washington Univ., St. Louis, MO, 63110, USA
SO Biochemical and Biophysical Research Communications (1988), 157(1), 81-6
CODEN: BBRCA9; ISSN: 0006-291X
DT Journal
LA English
CC 7-3 (Enzymes)
Section cross-reference(s): 32
AB [19-14C]androstenedione has been prepared and utilized as a substrate for assaying microsomal human placental aromatase. Enzyme activity is determined by measuring the rate at which [14C]formate is produced by aromatization of this 14C-labeled steroid. Isotope ratio expts. using

[19-14C]androstenedione and [1β-3H]androstenedione demonstrate that an apparent kinetic H isotope effect exists for the aromatization of the tritiated steroid with kH/kT ≈ 1.09. Metabolic switching occurs to a minor extent (≈3%) during aromatization of [1B-3H]androstenedione, but not during the aromatization of [19-14C]androstenedione.

ST androstenedione aromatase

IT Isotope effect
(in aromatization of androstenedione, by aromatase of human placenta, of carbon-14 and tritium)

IT 13864-55-6
RL: RCT (Reactant); RACT (Reactant or reagent)
(aromatization of, by aromatase of human placenta, reaction mechanism in relation to)

IT 9039-48-9, Aromatase
RL: ANT (Analyte); ANST (Analytical study)
(determination of, carbon-labeled androstenedione in, reaction mechanism in relation to)

IT 10028-17-8, Tritium, properties 14762-75-5, Carbon 14, properties
RL: PRP (Properties)
(isotope effect of, in aromatization of androstenedione by aromatase of human placenta)

IT 118790-73-1P, Androst-4-ene-3,17-dione-19-14C
RL: SPN (Synthetic preparation); PREP (Preparation)
(preparation and aromatase of human placenta determination using, reaction mechanism
in relation to)

IT 118790-74-2P, Androst-4-ene-3,17-dione-19-13C
RL: RCT (Reactant); SPN (Synthetic preparation); PREP (Preparation); RACT (Reactant or reagent)
(preparation and aromatization of, by aromatase of human placenta, reaction mechanism in relation to)

IT 106722-72-9 118790-75-3
RL: RCT (Reactant); RACT (Reactant or reagent)
(substitution reaction of, with epoxyestrane ethylene ketal)

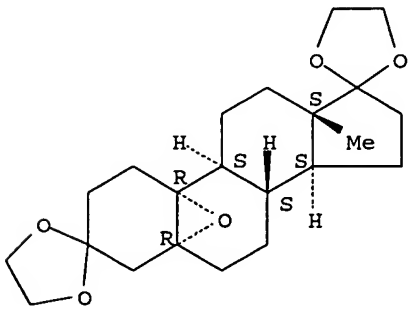
IT **102490-33-5**
RL: RCT (Reactant); RACT (Reactant or reagent)
(substitution reaction of, with labeled carbon methylmagnesium compds.)

IT **102490-33-5**
RL: RCT (Reactant); RACT (Reactant or reagent)
(substitution reaction of, with labeled carbon methylmagnesium compds.)

RN 102490-33-5 HCAPLUS

CN Estrane-3,17-dione, 5,10-epoxy-, cyclic bis(1,2-ethanediyl acetal), (5α,10α)- (9CI) (CA INDEX NAME)

Absolute stereochemistry.



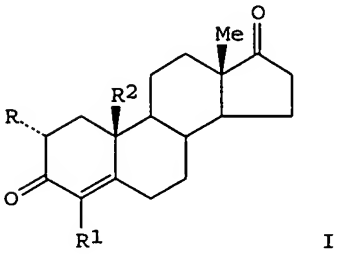
L25 ANSWER 5 OF 15 HCAPLUS COPYRIGHT 2005 ACS on STN

AN 1989:39230 HCAPLUS

DN 110:39230

ED Entered STN: 04 Feb 1989

TI Interactions of thiol-containing androgens with human placental aromatase
AU Bednarski, Patrick J.; Nelson, Sidney D.
CS Dep. Med. Chem., Univ. Washington, Seattle, WA, 98195, USA
SO Journal of Medicinal Chemistry (1989), 32(1), 203-13
CODEN: JMCMAR; ISSN: 0022-2623
DT Journal
LA English
CC 32-4 (Steroids)
Section cross-reference(s): 2
OS CASREACT 110:39230
GI

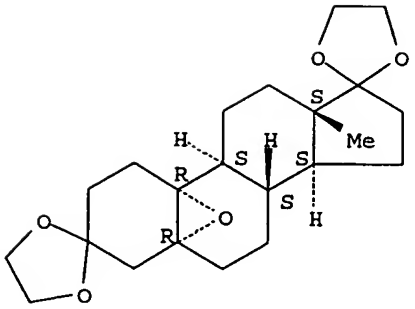


I

AB Androgens I (R = R1 = H, R2 = SH, CH2C.tplbond.CH; R = SH, R1 = H, R2 = Me; R = H, R1 = OH, R2 = Me) were synthesized and investigated to characterize structural features important for the inhibition of aromatase. Analogs of androstenedione with thiol groups in either the 2α,10β-, or 19-positions caused time-dependent inhibition of human placental aromatase. I (R = R1 = H, R2 = SH) proved to be the most potent suicide substrate. However, I (R = R1 = H, R2 = CH2SH) was the best all-around inhibitor. All the compds. except I (R = R1 = H, R2 = CH2SH) exhibited normal type IP-450 difference spectra with partially purified/solubilized, human placental aromatase. I (R = R1 = H, R2 = CH2SH) induced split Soret peaks at 380 and 474 nm, which suggested binding of the 19-thiolate directly to the Fe3+ of aromatase. This binding could be displaced by aminoglutethimide but not by androstenedione. The inhibitory activity of I (R = R1 = H, R2 = CH2SH) may be explained by two independent mechanisms, i.e. suicide inactivation of aromatase in the ferrous state, and a direct hyper-type II binding to the remaining portion of the cytochrome in the ferric state. A free thiol group was necessary for the suicide inhibitory activity of I (R = R1 = H, R2 = CH2SH). Aromatase previously inactivated by I could be reactivated after incubation with the disulfide reducing agent dithiothreitol, which suggests that a disulfide bond may be involved in aromatase inactivation by these inhibitors.
ST mercaptoandrosterone prepn aromatase inhibitor; androstenone mercapto prepn aromatase inhibitor
IT 90212-02-5
RL: RCT (Reactant); RACT (Reactant or reagent)
(acetylation and inhibition by, of human placental aromatase)
IT 3962-66-1, Estr-5(10)-ene-3,17-dione
RL: RCT (Reactant); RACT (Reactant or reagent)
(ketalization of)
IT 9039-48-9, Aromatase
RL: PROC (Process)
(of human placenta, inhibition of, by mercaptoandrostenones)
IT 63-05-8, Androst-4-ene-3,17-dione
RL: RCT (Reactant); RACT (Reactant or reagent)
(oxidation of)
IT 2220-74-8P
RL: RCT (Reactant); SPN (Synthetic preparation); PREP (Preparation); RACT (Reactant or reagent)
(preparation and bromination-hydroxylation of)

IT 117626-53-6P 117626-54-7P
RL: RCT (Reactant); SPN (Synthetic preparation); PREP (Preparation); RACT (Reactant or reagent)
(preparation and decarboxylation of)
IT 116168-70-8P
RL: RCT (Reactant); SPN (Synthetic preparation); PREP (Preparation); RACT (Reactant or reagent)
(preparation and dehydration of)
IT 116168-68-4P
RL: RCT (Reactant); SPN (Synthetic preparation); PREP (Preparation); RACT (Reactant or reagent)
(preparation and dehydrobromination of)
IT 7430-11-7P 17503-11-6P
RL: RCT (Reactant); SPN (Synthetic preparation); PREP (Preparation); RACT (Reactant or reagent)
(preparation and deoxygenation-hydroxylation of)
IT 117626-56-9P
RL: RCT (Reactant); SPN (Synthetic preparation); PREP (Preparation); RACT (Reactant or reagent)
(preparation and desilylation of)
IT 566-48-3P 77016-85-4P 90212-29-6P 116168-66-2P 117626-50-3P
RL: SPN (Synthetic preparation); PREP (Preparation)
(preparation and inhibition by, of human placental aromatase)
IT 116168-69-5P 117626-55-8P
RL: SPN (Synthetic preparation); PREP (Preparation)
(preparation and ketal cleavage of)
IT 13361-64-3P
RL: RCT (Reactant); SPN (Synthetic preparation); PREP (Preparation); RACT (Reactant or reagent)
(preparation and reaction of, with cuprous iodide)
IT 117678-49-6P
RL: RCT (Reactant); SPN (Synthetic preparation); PREP (Preparation); RACT (Reactant or reagent)
(preparation and reaction of, with epoxyestranedione)
IT 117626-51-4P 117626-52-5P
RL: RCT (Reactant); SPN (Synthetic preparation); PREP (Preparation); RACT (Reactant or reagent)
(preparation and reaction of, with xanthate)
IT **102490-33-5P**
RL: RCT (Reactant); SPN (Synthetic preparation); PREP (Preparation); RACT (Reactant or reagent)
(preparation and thiolysis of)
IT 571-16-4P 571-17-5P
RL: RCT (Reactant); SPN (Synthetic preparation); PREP (Preparation); RACT (Reactant or reagent)
(preparation and tosylation of)
IT 17689-04-2
RL: RCT (Reactant); RACT (Reactant or reagent)
(silylation of)
IT **102490-33-5P**
RL: RCT (Reactant); SPN (Synthetic preparation); PREP (Preparation); RACT (Reactant or reagent)
(preparation and thiolysis of)
RN 102490-33-5 HCAPLUS
CN Estrane-3,17-dione, 5,10-epoxy-, cyclic bis(1,2-ethanediyl acetal), (5α,10α)- (9CI) (CA INDEX NAME)

Absolute stereochemistry.



L25 ANSWER 6 OF 15 HCAPLUS COPYRIGHT 2005 ACS on STN
AN 1988:510745 HCAPLUS
DN 109:110745
ED Entered STN: 01 Oct 1988
TI Preparation of thiol-substituted steroids as suicide inhibitors of aromatase, useful in the treatment of breast cancer
IN Bednarski, Patrick J.; Porubek, David J.; Nelson, Sidney D.
PA Washington Research Foundation, USA
SO U.S., 14 pp.
CODEN: USXXAM
DT Patent
LA English
IC ICM A61K031-56
ICS C07J001-00
INCL 514170000
CC 32-4 (Steroids)
Section cross-reference(s): 1, 2, 7
FAN.CNT 1

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
PI US 4745109	A	19880517	US 1984-642620	19840820 <--
PRAI US 1984-642620		19840820 <--		

CLASS

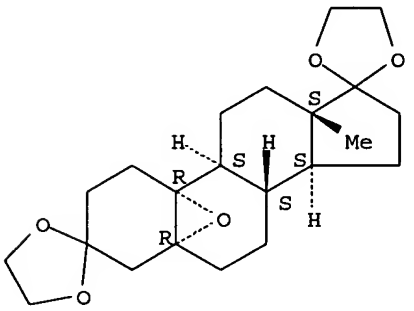
PATENT NO.	CLASS	PATENT FAMILY CLASSIFICATION CODES
US 4745109	ICM	A61K031-56
	ICS	C07J001-00
	INCL	514170000
US 4745109	NCL	514/170.000; 514/177.000; 552/523.000; 552/632.000; 552/644.000 <--

OS MARPAT 109:110745
GI For diagram(s), see printed CA Issue.
AB Title steroids I [R1 = thiol (e.g., SH or CH2SH); R2 = β-OH, oxo] were prepared and tested as suicide inhibitors of aromatase. 17β-Estradiol 3-Me ether underwent Birch reduction and subsequent hydrolysis to give 17β-hydroxyestr-5(10)-en-3-one, which was ketalized and acetylated to give 17β-acetoxyestr-5(10)-en-3-3-one ethylene ketal. The latter was converted to a bromohydrin, which was cyclized by NaOMe in MeOH to give the 5α(10α)-epoxide. Cleavage of the epoxide by NaSH and dehydration of the mercapto alc. gave I (R1 = SH, R2 = β-OH) (II). At 500 nM in a solution containing 1.0 mg human placental microsomal protein/mL and 0.36 mM NADPH, II reduced aromatase activity to 67% of control in 3 min at 30°, whereas 95-96% activity remained when either NADPH or atmospheric O was excluded.
ST thiol steroid prepn aromatase inhibitor; androstenedione mercapto prepn aromatase inhibitor; estrenone mercapto prepn aromatase inhibitor; suicide inhibitor aromatase steroid thiol
IT Estrogens
RL: BPN (Biosynthetic preparation); SPN (Synthetic preparation); BIOL (Biological study); PREP (Preparation)

(biosynthesis of, inhibitors of, steroidal thiols as)
IT Androgens
RL: PROC (Process)
(conversion of, to estrogens, steroidal thiols as inhibitors of)
IT Mammary gland, preparation
(neoplasm, estrogen-dependent)
IT Neoplasm inhibitors
(steroidal thiols)
IT Steroids, preparation
RL: SPN (Synthetic preparation); PREP (Preparation)
(mercapto, preparation of, from steroidal alcs.)
IT 1035-77-4
RL: RCT (Reactant); RACT (Reactant or reagent)
(Birch reduction of)
IT 510-64-5
RL: PROC (Process)
(conversion of, to thiol)
IT 1624-62-0
RL: RCT (Reactant); RACT (Reactant or reagent)
(ketalization of)
IT 28336-29-0P
RL: RCT (Reactant); SPN (Synthetic preparation); PREP (Preparation); RACT (Reactant or reagent)
(preparation and Birch reduction of)
IT 15342-09-3P
RL: RCT (Reactant); SPN (Synthetic preparation); PREP (Preparation); RACT (Reactant or reagent)
(preparation and acetylation of)
IT 95936-29-1P
RL: RCT (Reactant); SPN (Synthetic preparation); PREP (Preparation); RACT (Reactant or reagent)
(preparation and aminolysis of)
IT 2220-74-8P 18367-54-9P
RL: SPN (Synthetic preparation); PREP (Preparation)
(preparation and conversion of, to bromohydrin)
IT 28838-86-0P 116168-68-4P
RL: RCT (Reactant); SPN (Synthetic preparation); PREP (Preparation); RACT (Reactant or reagent)
(preparation and cyclization of, epoxide from)
IT 51101-79-2P 116168-70-8P
RL: RCT (Reactant); SPN (Synthetic preparation); PREP (Preparation); RACT (Reactant or reagent)
(preparation and dehydration of)
IT 51101-78-1P 116168-69-5P
RL: RCT (Reactant); SPN (Synthetic preparation); PREP (Preparation); RACT (Reactant or reagent)
(preparation and deketalization of)
IT 1238-30-8P 116168-67-3P
RL: RCT (Reactant); SPN (Synthetic preparation); PREP (Preparation); RACT (Reactant or reagent)
(preparation and hydrolysis of)
IT 1089-78-7P 3962-66-1P, Estr-5(10)-ene-3,17-dione
RL: RCT (Reactant); SPN (Synthetic preparation); PREP (Preparation); RACT (Reactant or reagent)
(preparation and ketalization of)
IT 95936-28-0P
RL: RCT (Reactant); SPN (Synthetic preparation); PREP (Preparation); RACT (Reactant or reagent)
(preparation and substitution reaction of, with potassium Et xanthogenate)
IT 24275-29-4P 102490-33-5P
RL: RCT (Reactant); SPN (Synthetic preparation); PREP (Preparation); RACT (Reactant or reagent)
(preparation and sulfurization of)
IT 51101-80-5P 90212-02-5P 116168-66-2P
RL: SPN (Synthetic preparation); PREP (Preparation)
(preparation of, as suicide inhibitor of aromatase)

IT 63-05-8, Androstenedione
RL: RCT (Reactant); RACT (Reactant or reagent)
(protection of aromatase from steroidal thiol suicide inhibitors by)
IT 140-89-6, Potassium ethyl xanthogenate
RL: RCT (Reactant); RACT (Reactant or reagent)
(substitution reaction of, with triflyloxyandrostenedione)
IT 7782-44-7, Oxygen, uses and miscellaneous
RL: USES (Uses)
(suicide inhibition of aromatase by steroidal thiols in presence of)
IT 53-57-6, NADPH
RL: RCT (Reactant); RACT (Reactant or reagent)
(suicide inhibition of aromatase by steroidal thiols in presence of)
IT 52-90-4, L-Cysteine, uses and miscellaneous
RL: USES (Uses)
(suicide inhibition of aromatase by steroidal thiols, effect on)
IT 9039-48-9, Aromatase
RL: RCT (Reactant); RACT (Reactant or reagent)
(suicide inhibition of, by steroidal thiols)
IT **102490-33-5P**
RL: RCT (Reactant); SPN (Synthetic preparation); PREP (Preparation); RACT (Reactant or reagent)
(preparation and sulfurization of)
RN 102490-33-5 HCAPLUS
CN Estrane-3,17-dione, 5,10-epoxy-, cyclic bis(1,2-ethanediyl acetal), (5α,10α)- (9CI) (CA INDEX NAME)

Absolute stereochemistry.



L25 ANSWER 7 OF 15 HCAPLUS COPYRIGHT 2005 ACS on STN
AN 1986:515283 HCAPLUS
DN 105:115283
ED Entered STN: 03 Oct 1986
TI Transition metal phthalocyanines and iodosobenzene as epoxidizing agents
IN Rohde, Ralph; Neef, Guenter
PA Schering A.-G. , Fed. Rep. Ger.
SO Ger. Offen., 13 pp.
CODEN: GWXXBX
DT Patent
LA German
IC ICM C07B041-04
ICS C07J071-00; C07D301-03; C09B067-12
CC 32-3 (Steroids)
Section cross-reference(s): 25, 26
FAN.CNT 1

	PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
PI	DE 3438484	A1	19860417	DE 1984-3438484	19841017 <--
	DE 3438484	C2	19870619		
PRAI	DE 1984-3438484		19841017 <--		

CLASS
PATENT NO. CLASS PATENT FAMILY CLASSIFICATION CODES

DE 3438484	ICM	C07B041-04
	ICS	C07J071-00; C07D301-03; C09B067-12

AB Transition metal phthalocyanines and PhIO were used as epoxidizing agents of organic acyclic, cyclic or polycyclic compds. containing ≥1 C:C double bond, to give an epoxidized compound A solution of 3,3-(2,2-dimethyltrimethylenedioxy)-5(10),9(11)-estradien-17-one in MeCN was treated with PhIO and Fe phthalocyanines and the mixture stirred 3.5 h at room temperature to give 6.7% 3,3-(2,2-dimethyltrimethylenedioxy)-5β,10β-epoxy-9(11)-estren-17-one and 73.7% the 5α,10α-epoxy isomer.

ST steroid epoxidn phthalocyanine iodosobenzene; double bond epoxidn phthalocyanine iodosobenzene; epoxyestrenone; estrenone epoxy

IT Epoxidation
(agents for, transition metal phthalocyanines and iodosobenzene as)

IT Steroids, reactions
RL: RCT (Reactant); RACT (Reactant or reagent)
(unsatd., epoxidn. of, with transition metal phthalocyanines and iodosobenzene)

IT 55534-06-0 104000-03-5 104000-06-8 104000-08-0 104068-75-9
RL: RCT (Reactant); RACT (Reactant or reagent)
(epoxidn. of, with iodosobenzene and iron phthalocyanine)

IT 91175-92-7
RL: RCT (Reactant); RACT (Reactant or reagent)
(epoxidn. of, with iodosobenzene and transition metal phthalocyanines)

IT 132-16-1 574-93-6D, transition metal derivs. 3317-67-7 14055-02-8 14325-24-7
RL: RCT (Reactant); RACT (Reactant or reagent)
(iodosobenzene and, epoxidizing agent for unsatd. steroids)

IT 93697-60-0P 104000-04-6P **104000-05-7P** 104000-07-9P 104000-09-1P 104068-76-0P 104068-77-1P 104068-78-2P
RL: SPN (Synthetic preparation); PREP (Preparation)
(preparation of, by epoxidn. of unsatd. steroid with iodosobenzene and iron phthalocyanine)

IT 98049-51-5P 104000-02-4P
RL: SPN (Synthetic preparation); PREP (Preparation)
(preparation of, with iodosobenzene and transition metal phthalocyanines)

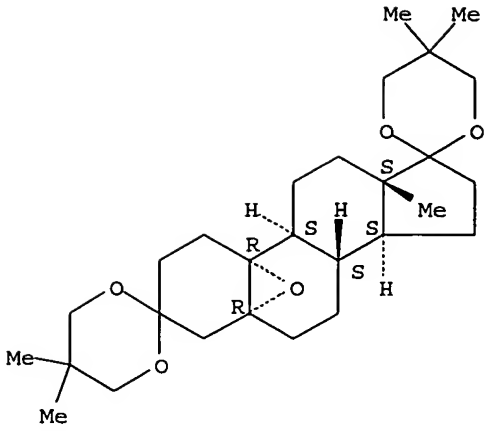
IT 536-80-1
RL: RCT (Reactant); RACT (Reactant or reagent)
(transition metal phthalocyanines and, epoxidizing agents for unsatd. steroids)

IT **104000-05-7P**
RL: SPN (Synthetic preparation); PREP (Preparation)
(preparation of, by epoxidn. of unsatd. steroid with iodosobenzene and iron phthalocyanine)

RN 104000-05-7 HCAPLUS

CN Estrane-3,17-dione, 5,10-epoxy-, cyclic bis(2,2-dimethyl-1,3-propanediyl acetal), (5α,10α)- (9CI) (CA INDEX NAME)

Absolute stereochemistry.



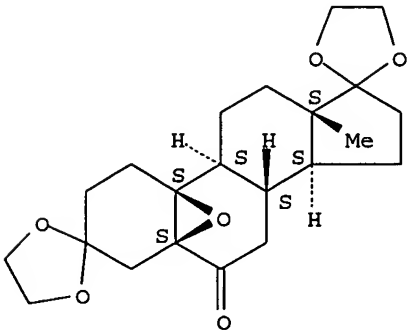
L25 ANSWER 8 OF 15 HCAPLUS COPYRIGHT 2005 ACS on STN
AN 1982:406614 HCAPLUS
DN 97:6614
ED Entered STN: 12 May 1984
TI Selective aromatization of ring B in 19-norsteroids and synthesis of equilenin-type compounds
AU Mihailovic, Mihailo L.; Forsek, Joze; Lorenc, Ljubinka
CS Dep. Chem., Univ. Belgrade, Belgrade, YU-11001, Yugoslavia
SO Journal of the Chemical Society, Perkin Transactions 1: Organic and Bio-Organic Chemistry (1972-1999) (1982), (1), 1-7
CODEN: JCPRB4; ISSN: 0300-922X
DT Journal
LA English
CC 32-3 (Steroids)
OS CASREACT 97:6614
GI

* STRUCTURE DIAGRAM TOO LARGE FOR DISPLAY - AVAILABLE VIÀ OFFLINE PRINT *

AB Acetoxyepoxyestranone I (R2 = β-O, R1R2 = O, R3 = OAc, R4 = α-H), prepared from I (R2 = bond, R1 = R3 = R4 = H, R2 = OH), by sequential stereoselective epoxidn., oxidation, and stereoselective acetoxylation, underwent selective aromatization of ring B in MeOH/OH- under reflux for 1 h to give estratrienediol II. II underwent sequential diacetylation, bisdeacetalization, and ring A aromatization with Pb(OAc)4 to give 6,7-diacetoxyequilenin (III).
ST norsteroid selective aromatization; acetoxyequilenin; equilenin acetoxy; epoxyestranone selective aromatization; estranone epoxy selective aromatization
IT 19-Norsteroids
RL: RCT (Reactant); RACT (Reactant or reagent)
(7α-acetoxy-5β,10β-epoxy-6-oxo, selective aromatization of ring A of)
IT Aromatization
(of acetoxyepoxyestranone, selective ring B)
IT 17324-86-6
RL: RCT (Reactant); RACT (Reactant or reagent)
(epoxidn. of, stereoselective)
IT **1103-94-2P**
RL: RCT (Reactant); SPN (Synthetic preparation); PREP (Preparation); RACT (Reactant or reagent)
(preparation and acetoxylation of)

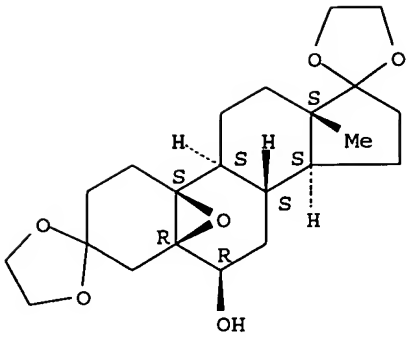
IT 69660-94-2P 69660-97-5P
RL: RCT (Reactant); SPN (Synthetic preparation); PREP (Preparation); RACT (Reactant or reagent)
(preparation and acetylation of)
IT 69660-95-3P
RL: RCT (Reactant); SPN (Synthetic preparation); PREP (Preparation); RACT (Reactant or reagent)
(preparation and deacetalization of)
IT 81969-02-0P
RL: RCT (Reactant); SPN (Synthetic preparation); PREP (Preparation); RACT (Reactant or reagent)
(preparation and oxidation of)
IT 69660-96-4P 69660-99-7P
RL: RCT (Reactant); SPN (Synthetic preparation); PREP (Preparation); RACT (Reactant or reagent)
(preparation and ring A aromatization of)
IT 81901-75-9P 81901-76-0P
RL: RCT (Reactant); SPN (Synthetic preparation); PREP (Preparation); RACT (Reactant or reagent)
(preparation and selective ring B aromatization of)
IT 69660-98-6P
RL: SPN (Synthetic preparation); PREP (Preparation)
(preparation of)
IT 2208-12-0P
RL: SPN (Synthetic preparation); PREP (Preparation)
(preparation of, by aromatization of ring A of epoxyestranol)
IT 69660-93-1P
RL: RCT (Reactant); SPN (Synthetic preparation); PREP (Preparation); RACT (Reactant or reagent)
(preparation, saponification, and selective ring B aromatization of)
IT 1103-94-2P
RL: RCT (Reactant); SPN (Synthetic preparation); PREP (Preparation); RACT (Reactant or reagent)
(preparation and acetoxylation of)
RN 1103-94-2 HCAPLUS
CN Estrane-3,6,17-trione, 5,10-epoxy-, cyclic 3,17-bis(1,2-ethanediyl acetal), (5β)- (9CI) (CA INDEX NAME)

Absolute stereochemistry.



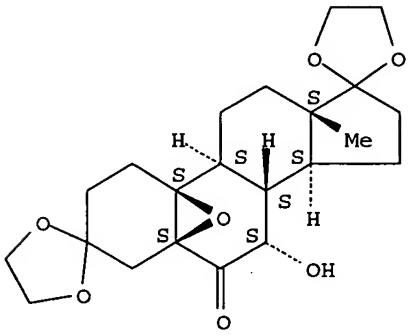
IT 81969-02-0P
RL: RCT (Reactant); SPN (Synthetic preparation); PREP (Preparation); RACT (Reactant or reagent)
(preparation and oxidation of)
RN 81969-02-0 HCAPLUS
CN Estrane-3,17-dione, 5,10-epoxy-6-hydroxy-, cyclic bis(1,2-ethanediyl acetal), (5β,6β)- (9CI) (CA INDEX NAME)

Absolute stereochemistry.



IT **81901-75-9P 81901-76-0P**
RL: RCT (Reactant); SPN (Synthetic preparation); PREP (Preparation); RACT (Reactant or reagent)
(preparation and selective ring B aromatization of)
RN 81901-75-9 HCAPLUS
CN Estrane-3,6,17-trione, 5,10-epoxy-7-hydroxy-, cyclic 3,17-bis(1,2-ethanediyl acetal), (5β,7α)- (9CI) (CA INDEX NAME)

Absolute stereochemistry.

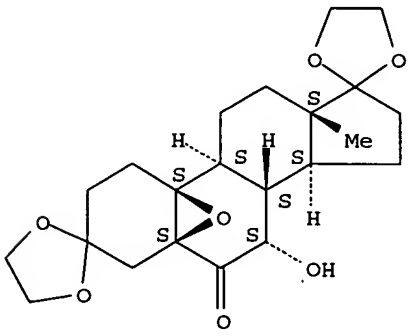


RN 81901-76-0 HCAPLUS
CN Estrane-3,6,17-trione, 5,10-epoxy-7-hydroxy-, cyclic 3,17-bis(1,2-ethanediyl acetal), dimer (9CI) (CA INDEX NAME)

CM 1

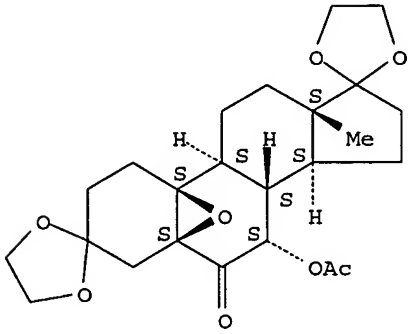
CRN 81901-75-9
CMF C22 H30 O7

Absolute stereochemistry.

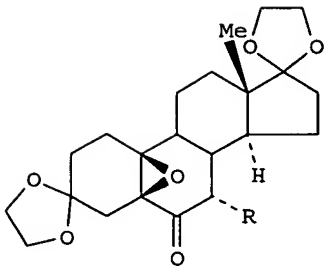


IT 69660-93-1P
RL: RCT (Reactant); SPN (Synthetic preparation); PREP (Preparation); RACT (Reactant or reagent)
(preparation, saponification, and selective ring B aromatization of)
RN 69660-93-1 HCAPLUS
CN Estrane-3,6,17-trione, 7-(acetyloxy)-5,10-epoxy-, cyclic 3,17-bis(1,2-ethanediyl acetal), (5β,7α)- (9CI) (CA INDEX NAME)

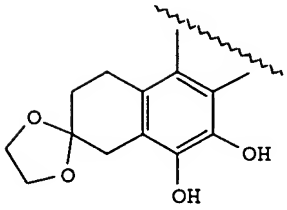
Absolute stereochemistry.



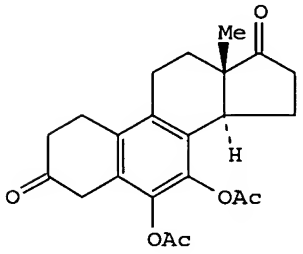
L25 ANSWER 9 OF 15 HCAPLUS COPYRIGHT 2005 ACS on STN
AN 1979:152450 HCAPLUS
DN 90:152450
ED Entered STN: 12 May 1984
TI New approach to the aromatization of ring B in 19-norsteroids and to the synthesis of equilenin-type compounds
AU Mihailovic, Mihailo Lj.; Forsek, Joze; Lorenc, Ljubinka
CS Dep. Chem., Univ. Belgrade, Belgrade, Yugoslavia
SO Journal of the Chemical Society, Chemical Communications (1978), (21), 916-18
CODEN: JCCCAT; ISSN: 0022-4936
DT Journal
LA English
CC 32-3 (Steroids)
GI



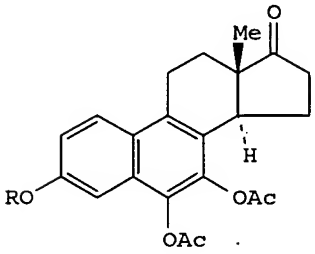
I



II



III



IV

AB Heating estranone I (R = OAc), prepared (50-60%) by Pb(OAc)4 acetoxylation of I (R = H), in alkali gave 80% estratrienediol II with retention of the C-14 configuration. Sequential acetylation (92%) deacetalization (85%), and Pb(OAc)4 aromatization of the resulting diketone III gave 6,7-diacetoxyequilenin IV (R = H). Acetylation of the latter gave triacetate IV (R = Ac) in 50% overall yield from III.

ST aromatization epoxyestranone equilenin prepn; estranone epoxy aromatization

IT 19-Norsteroids
RL: RCT (Reactant); RACT (Reactant or reagent)
(aromatization of ring B of, equilenin-type compds. by)

IT Aromatization
(of 19-norsteroids, equilenin-type compds. by)

IT **1103-94-2**
RL: RCT (Reactant); RACT (Reactant or reagent)
(acetoxylation of)

IT 69660-94-2P 69660-97-5P
RL: RCT (Reactant); SPN (Synthetic preparation); PREP (Preparation); RACT (Reactant or reagent)
(preparation and acetylation of)

IT **69660-93-1P** 69660-96-4P
RL: RCT (Reactant); SPN (Synthetic preparation); PREP (Preparation); RACT (Reactant or reagent)
(preparation and aromatization of)

IT 69660-95-3P
RL: RCT (Reactant); SPN (Synthetic preparation); PREP (Preparation); RACT (Reactant or reagent)
(preparation and deacetalization of)

IT 69660-99-7P
RL: RCT (Reactant); SPN (Synthetic preparation); PREP (Preparation); RACT (Reactant or reagent)
(preparation and dehydrogenation of)

IT 69660-98-6P
RL: SPN (Synthetic preparation); PREP (Preparation)
(preparation of, by aromatization of ring B in 19-norsteroids)

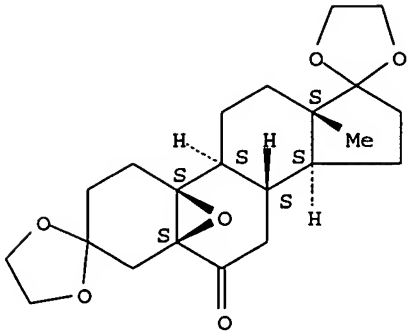
IT **1103-94-2**
RL: RCT (Reactant); RACT (Reactant or reagent)
(acetoxylation of)

RN 1103-94-2 HCAPLUS

CN Estrane-3,6,17-trione, 5,10-epoxy-, cyclic 3,17-bis(1,2-ethanediyl

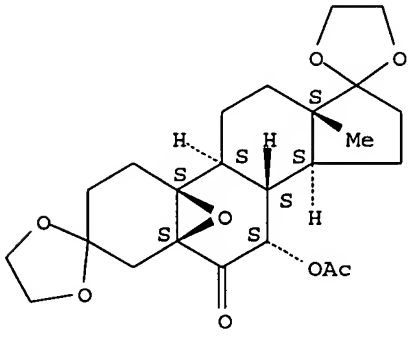
acetal), (5β)- (9CI) (CA INDEX NAME)

Absolute stereochemistry.



IT 69660-93-1P
RL: RCT (Reactant); SPN (Synthetic preparation); PREP (Preparation); RACT (Reactant or reagent)
(preparation and aromatization of)
RN 69660-93-1 HCAPLUS
CN Estrane-3,6,17-trione, 7-(acetyloxy)-5,10-epoxy-, cyclic 3,17-bis(1,2-ethanediyl acetal), (5β,7α)- (9CI) (CA INDEX NAME)

Absolute stereochemistry.



L25 ANSWER 10 OF 15 HCAPLUS COPYRIGHT 2005 ACS on STN
AN 1965:403500 HCAPLUS
DN 63:3500
OREF 63:655g-h,656a-h,657a-b
ED Entered STN: 22 Apr 2001
TI Preparation of phenolic steroids and their ethers
IN Ercoli, Alberto; Gardi, Rinaldo; Pedrali, Cesare
PA Francesco Vesmara, Societa per Azioni
SO 34 pp.
DT Patent
LA Unavailable
CC 42 (Steroids)
FAN.CNT 1

	PATENT NO.	KIND	DATE	APPLICATION NO.	DATE	
PI	BE 641351		19640616	BE		<--
	DE 1223379			DE		
	FR 1394051			FR		
	NL 302028			NL		
	US 3231567		1966	US		<--

Search done by Noble Jarrell

PRAI IT 19621219 <--
CLASS

PATENT NO.	CLASS	PATENT FAMILY CLASSIFICATION CODES
US 3231567	NCL	540/008.000; 204/157.830; 540/010.000; 540/025.000; 540/037.000; 540/076.000; 552/558.000; 552/583.000; 552/606.000; 552/615.000; 552/625.000; 552/630.000; 552/631.000; 552/632.000 <--

AB Treatment of 5,6- and 5,10-disubstituted 3-oxo-19-nor steroids (epoxides, halohydrins, dihalides, dihydroxides) with strong acids leads to ring A aromatic compds. (phenols). In the presence of alcs., phenolic ethers are obtained. A mixture of 3,3:17,17-bis(ethylenedioxy)-19-norandrost-5(6)-ene (I) and norandrost-5(10)-ene (II) (2 g.) (obtained by reduction of 3,3:17,17-bis(ethylenedioxy)-10β-cyano-19-norandrost-5(6)-ene with Na and EtOH) was dissolved in 200 ml. Et2O and treated with 20 ml. 15% monoperphthalic acid solution After standing overnight and washing with 5% NaHCO3, saturated NaCl solution, and H2O, the solution was dried, evaporated in vacuo, and the residue chromatographed on Florisil to give 1.35 g. 3,3:17,17-bis(ethylenedioxy)-5β,10β-oxido-19-norandrostane (III), m. 116-17° (MeOH and C6H14), [α]25D 10° (CHCl3) (eluted with 3:2 C6H6-Et2O), 0.1 g. 3,3:17,17-bis(ethylenedioxy)-5α,10α-oxido-19-norandrostane (IV), m. 120-1°, [α]25D 20° (CHCl3), and 0.37 g. 3,3:17,17-bis(ethylenedioxy)-5α,6α-oxido-19-norandrostane (V), m. 190-1°, [α]25D -41° (CHCl3) (eluted with 1:1 C6H6-Et2O). A solution of 1 g. III in 5 ml. Me2CO and 2 drops concentrated HCl was refluxed 2 hrs., concentrated in vacuo, and diluted with H2O to give 0.58 g. estrone (VI), m. 253-5°. Similarly, VI was obtained from IV. Reaction of 100 mg. V in 5 ml. AcOH with dry HCl gas during 2 hrs. and dilution with H2O gave 46 mg. VI. The crude mixture of III, IV, and V obtained from 2 g. I + II was dissolved in 20 ml. Me2CO and 1 ml. concentrated HCl and refluxed 2 hrs. to give VI, m. 258-60°. VI was also prepared by acid treatment of 5β,10β-oxido-19-norandrostane-3,17-dione (HCl) and 5α-hydroxy-6β-bromo-19-norandrostane-3,17-dione [(CO2H)2]. A solution of 100 mg. III in 5 ml. MeOH and 2 drops concentrated HCl was refluxed 1/2 hr., concentrated, diluted with H2O, and the precipitate recrystd. from MeOH to give VI methyl ether (VII), m. 169-70°, [α]25D 162° (CHCl3). VII was also obtained by refluxing 70 mg. 5α-bromo-10β-hydroxy-19-norandrostane-3,17-dione 1/2 hr. in 5 ml. MeOH (yield 49 mg., m. 168-9° (MeOH)) (no acid added), by refluxing 100 mg. 5α,10β-dibromo-19-norandrostane-3,17-dione in 5 ml. C6H6 and 1 ml. MeOH 1/2 hr. (yield 55 mg.) (no acid added), by refluxing 100 mg. 5α,6β-dihydroxy-19-norandrostane-3,17-dione in 5 ml. MeOH and 2 drops concentrated HCl 1/2 hr. (yield 46 mg.), and similarly from 100 mg. 5α-hydroxy-6β-fluoro-19-norandrostane-3,17-dione (yield 100%). A solution of 100 mg. III in 5 ml. cyclopentanol and 2 drops concentrated HCl was refluxed 1 hr. and evaporated in vacuo. The residue was crystallized from MeOH to give 42 mg. VI cyclopentyl ether (VIII), m. 152-3° (MeOH), [α]25D 136° (dioxane). Similarly, 100 mg. 5α,10β-dihydroxy-19-norandrostane-3,17-dione gave 64 mg. VIII, and 100 mg. 5α-hydroxy-10β-bromo-19-norandrostane-3,17-dione, heated 1 hr. with 5 ml. cyclopentanol and 0.5 ml. HCO2H, yielded 42 mg. VIII. When 200 mg. V was refluxed 2 hrs. in 10 ml. cyclohexanol and concentrated HCl, VI cyclohexyl ether, m. 156-7°, [α]25D 134° (dioxane), was obtained, while III in PhCH2OH gave 80% VI benzyl ether, m. 129-30°, [α]25D 132° (dioxane). A solution of 1 g. V in 20 ml. Me2CO, 0.5 g. cetyl alc., and 2 drops concentrated HCl was refluxed 2 hrs. to give VI cetyl ether (IX), m. 67-8°, [α]25D 95° (dioxane). Similarly prepared were VI nonyl ether, m. 56-8°, [α]25D 114° (dioxane) and VI ethyl ether, m. 126°, [α]25D 150° (dioxane). IX was also obtained from 5α-bromo-6β-hydroxy-19-norandrostane-3,17-dione. Similarly, 1 g. 5α,6β-dibromo-19-norandrostane-3,17-dione in 20 ml. Me2CO, 0.5 g. cinnamyl alc., and 0.2 ml. concentrated HCl gave VI cinnamyl ether, m. 144-5°. Also prepared was VI allyl ether, m.

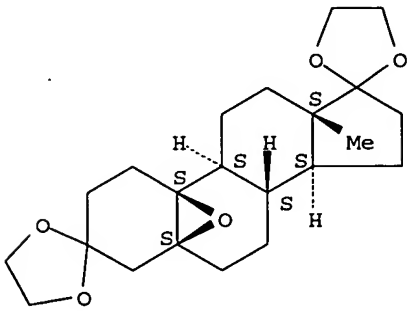
107-8°, [α]25D 144° (dioxane). A solution of 5β,10β-oxido-17β-hydroxy-19-norandrostan-3-one in 5 ml. Me2CO and 2 drops concentrated HCl was refluxed 1/2 hr. and diluted with H2O to give estradiol which was also prepared from 6β-fluoro-5α,17β-dihydroxy-19-norandrostan-3-one. A solution of 2 g. 3,3-ethylenedioxy-17α-ethynyl-17β-hydroxy-19-norandrost-5-ene in 150 ml. Et2O was treated with 10 ml. 20% PhCO3H solution After standing overnight, washing with 5% NaHCO3, saturated NaCl solution, and H2O, and evaporation, the residue was dissolved in 20 ml. cyclopentanol and 1 ml. concentrated HCl, and the solution refluxed 2 hrs. and diluted with H2O to give 17α-ethynylestradiol 3-cyclopentyl ether (X), m. 107-8°, [α]25D 5° (dioxane). Similarly prepared were the cyclopentyl ethers of 17α-methylestradiol, m. 107-8°, [α]22D 45° (dioxane), and of 17α-ethylestradiol, m. 122-4°, [α]22D 43.5° (dioxane). X was also obtained from 10β-fluoro-5α, 17β-dihydroxy-17α-ethynyl-19-norandrostan-3-one. When 2 g. 3,3-ethylenedioxy-5β,10β-oxido-17α-ethynyl-17β-hydroxy-19-norandrostane were refluxed 1/2 hr. in 20 ml. MeOH with 30 mg. MeC6H4SO3H, 17α-ethynylestradiol 3-methyl ether (XI) was obtained. Similarly, 100 mg. 3,3-ethylenedioxy-5α-fluoro-10β,17β-dihydroxy-17α-ethynyl-19-norandrostane in MeOH and HCl (1/2 hr. reflux) gave 76 mg. XI, m. 150-1°, [α]25D 2.3° (dioxane). A solution of 2 g. of a mixture of 3,3:20,20-bis(ethylenedioxy)-19-norpregn-5(6)-ene and norpregn-5(10)-ene (obtained by reduction of 3,3:20,20-bis(ethylenedioxy)-10β-cyano-19-norpregn-5(6)-ene with Na and EtOH) in 200 ml. Et2O was treated with 60 ml. 15% monoperphthalic acid as described for III, IV, and V. The crude reaction product (.apprx.2 g.) was dissolved in 15 ml. Me2CO and 0.5 ml. H2SO4 and refluxed 2 hrs. Evaporation in vacuo and dilution with H2O gave 0.6 g. 3-hydroxy-17-acetylestra-1,3,5(10)-triene (XII), m. 247-9°, [α]25D 159° (CHCl3). The epoxides prepared in the preceding experiment were separated by chromatography on Florisil to give (elution with 3:2 C6H6Et2O) 3,3:20,20-bis(ethylenedioxy)-5β,10β-oxido-19-norpregnane (XIII), m. 136-7°, [α]25D 58° (CHCl3), and 3,3:20,20-bis(ethylenedioxy)-5α,6α-oxido-19-norpregnane (XIV) (not characterized). Refluxing 1 g. XIII 2 hrs. in 5 ml. Me2CO and 2 drops H2SO4, concentration in vacuo, and dilution with H2O gave 0.6 g. XII. Similarly, 1 g. XIV in 50 ml. AcOH treated 2 hrs. with HCl gas and dilution with H2O gave 450 mg. XII. A solution of 1 g. 10β-fluoro-5α-hydroxy-19-norpregnane-3,20-dione in 5 ml. Me2CO was refluxed 2 hrs. with 20 mg. sulfosalicylic acid and gave 0.6 g. XII. When 0.5 g. XIII was dissolved in 25 ml. MeOH and 2 drops concentrated HCl, the solution kept 1 hr. at room temperature and diluted with H2O, and the precipitate recrystd. from MeOH, XII methyl ether, m. 134-6°, [α]25D 160° (CHCl3), was obtained. Reaction of 5α-chloro-10β-hydroxy-19-norpregnane-3,20-dione with cyclopentanol and concentrated HCl (ratio 20:1) (2 hrs. reflux) gave XII cyclopentyl ether, m. 116-17°, [α]25D 138° (dioxane). The crude epoxides obtained from 850 mg. 3,3-ethylenedioxy-17α-acetoxy-19-norpregn-5-en-20-one in 80 ml. Et2O and 5 ml. 15% monoperphthalic acid in Et2O were dissolved in 15 ml. Me2CO and 0.5 ml. concentrated HCl and refluxed 2 hrs. to give, after evaporation and dilution with H2O, 3-hydroxy-17α-acetoxy-17β-acetylestra-1,3,5(10)-triene, m. 242-4°, [α]25D 49° (CHCl3). A solution of 1 g. 3,3:20,20-bis(ethylenedioxy)-17α-hydroxy-19-norpregn-5-ene in 50 ml. Et2O was treated with 15 ml. PhCO3H solution The crude mixture of epoxides was refluxed 2 hrs. in 15 ml. Me2CO and 0.5 ml. H2SO4 to give 3,17α-dihydroxy-17β-acetylestra-1,3,5(10)-triene (XV), m. 240-2°, [α]25D 90.5° (dioxane). From the mixture of epoxides, the 5β,10β-oxido compound was separated by recrystn. from MeOH, and 1 g. was refluxed 1/2 hr. in 50 ml. MeOH with 100 mg. MeC6H4SO3H to give XV methyl ether, m. 150-2° (MeOH), [α]25D 45.5° (dioxane). Ir spectra are reported for III, IV, and V.

IT Steroids
(3-hydroxy Δ1,3,5(10)-, and ethers thereof)

IT Spectra, infrared
(of 5,10-epoxy-5α-estrane-3,17-dione cyclic bis(ethylene acetal)

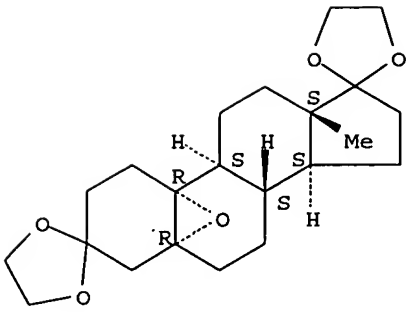
and related compds.)
IT 5α-Estrae-3,17-dione, 5,6α-epoxy-, cyclic bis(ethylene acetal)
IT 72-33-3, 19-Nor-17α-pregna-1,3,5(10)-trien-20-yn-17-ol, 3-methoxy- 152-43-2, 19-Nor-17α-pregna-1,3,5(10)-trien-20-yn-17-ol, 3-(cyclopentyloxy)- 858-98-0, Estra-1,3,5(10-trien-17-one, 3-(benzyloxy)- 1474-50-6, Estra-1,3,5(10-trien-17-one, 3-ethoxy- 1624-56-2, 19-Norpregna-1,3,5(10)-trien-20-one, 3-(cyclopentyloxy)- 1624-57-3, 19-Norpregna-1,3,5(10)-trien-20-one, 3,17-dihydroxy- 1624-58-4, 19-Norpregna-1,3,5(10)-trien-20-one, 17-hydroxy-3-methoxy- **1624-60-8**, 5β-Estrane-3,17-dione, 5,10-epoxy-, cyclic bis(ethylene acetal) 1624-62-0, Estra-1,3,5(10-trien-17-one, 3-methoxy- 1624-63-1, Estra-1,3,5(10-trien-17-one, 3-(cyclohexyloxy)- 1624-64-2, Estra-1,3,5(10-trien-17-one, 3-(nonyloxy)- 1624-66-4, Estra-1,3,5(10-trien-17-one, 3-(cinnamyloxy)- 1624-67-5, Estra-1,3,5(10-trien-17-one, 3-(allyloxy)- 1624-69-7, Estra-1,3,5(10)-trien-17β-ol, 3-(cyclopentyloxy)-17-methyl- 1624-70-0, 19-Nor-17α-pregna-1,3,5(10)-trien-17-ol, 3-(cyclopentyloxy)- 1624-72-2, 19-Nor-5β-pregnane-3,20-dione, 5,10-epoxy-, cyclic bis(ethylene acetal) 1624-73-3, 19-Norpregna-1,3,5(10)-trien-20-one, 3-methoxy- 1624-74-4, 19-Norpregna-1,3,5(10)-trien-20-one, 3,17-dihydroxy-, 17-acetate 1624-75-5, Pregn-4-ene-3,20-dione, 6α-amino- 1667-98-7, 19-Norpregna-1,3,5(10)-trien-20-one, 3-hydroxy- 1805-17-0, Estra-1,3,5(10-trien-17-one, 3-(hexadecyloxy)- 1852-81-9, Estra-1,3,5(10-trien-17-one, 3-(cyclopentyloxy)- 2027-44-3, Pregn-4-ene-3,20-dione, 6β-acetamido- 2454-33-3, Pregn-4-ene-3,20-dione, 6α-acetamido- **102490-33-5**, 5α,10α-Estrane-3,17-dione, 5,10-epoxy-, cyclic bis(ethylene acetal)
(preparation of)
IT 166-68-7, Dispiro[1,3-dioxolane-2,3'(4'H)-[5,10]epoxy[17H]cyclopenta[a]phenanthrene-17',2''-[1,3]dioxolane] 175-26-8, Dispiro[1,3-dioxolane-2,3'(4'H)-[5,6]epoxy[5H]cyclopenta[a]phenanthrene-17'(2'H),2''-[1,3]dioxolane]
(steroid derivs.)
IT **1624-60-8**, 5β-Estrane-3,17-dione, 5,10-epoxy-, cyclic bis(ethylene acetal) **102490-33-5**, 5α,10α-Estrane-3,17-dione, 5,10-epoxy-, cyclic bis(ethylene acetal)
(preparation of)
RN 1624-60-8 HCAPLUS
CN Estrane-3,17-dione, 5,10-epoxy-, cyclic bis(1,2-ethanediyl acetal), (5β)- (9CI) (CA INDEX NAME)

Absolute stereochemistry.



RN 102490-33-5 HCAPLUS
CN Estrane-3,17-dione, 5,10-epoxy-, cyclic bis(1,2-ethanediyl acetal), (5α,10α)- (9CI) (CA INDEX NAME)

Absolute stereochemistry.



L25 ANSWER 11 OF 15 HCAPLUS COPYRIGHT 2005 ACS on STN
AN 1965:403499 HCAPLUS
DN 63:3499
OREF 63:655e-g
ED Entered STN: 22 Apr 2001
TI 20-Oxo-16-pregnene derivatives
IN Magyar, Gyorgy; Bite, Pal
PA Gedeon Richter Vegyeszeti Gyar R. T.
SO 3 pp.
DT Patent
LA Unavailable
CC 42 (Steroids)
FAN.CNT 1

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE	
PI AT 239970		19650510	AT		<--
PRAI HU		19600323	<--		

CLASS

PATENT NO.	CLASS	PATENT FAMILY CLASSIFICATION CODES

AB In a process for preparing 20-oxo-16-pregnene derivs. from steroid sapogenins or from solanum alkaloids the starting compound is acylated, isomerized, oxidized, and the δ-acyloxy- or δ-acylaminoisocaprolonate group is removed by treatment with a mineral acid at elevated temperature in the presence of a H2O-immiscible organic solvent, e.g. benzene, toluene, xylene, dichloroethylene, the mineral acid being used in an amount of ≤5% by weight of the reaction product. Preferably, benzene is used as solvent, and the cleavage is effected at the b.p. of the reaction mixture and with 1-3% concentrated HCl. Thus, using solasodine as starting material, 5,16-pregnadien-3β-ol-20-one acetate, m. 170-2°, and 5,16-pregnadienolone propionate, m. 172-4°, were obtained. From tomatidine, 5α-pregn-16-en-3β-ol-20-one acetate, m. 163-4°, and the resp. propionate, m. 182-4°, were obtained. Diosgenine was also used as starting material to obtain the acetate and propionate of 15,16-pregnadienolone. The compds. are useful as intermediates in the manufacture of steroid hormones.

IT Steroids
(20-keto Δ16-, from sapogenins and solanum alkaloids)
IT Solanum
(alkaloids, pregn-16-en-20-one derivative preparation from)
IT Sapogenins
(pregn-16-en-20-one derivs. from)
IT 979-02-2, Pregna-5,16-dien-20-one, 3β-hydroxy-, acetate 1169-20-6, 5α-Pregn-16-en-20-one, 3β-hydroxy-, acetate 1624-98-2, 5α-Pregn-16-en-20-one, 3β-hydroxy-, propionate 3285-87-8, Pregna-5,16-dien-20-one, 3β-hydroxy-, propionate
(preparation of)

L25 ANSWER 12 OF 15 HCAPLUS COPYRIGHT 2005 ACS on STN
AN 1965:3268 HCAPLUS

DN 62:3268
OREF 62:621c-h,622a
ED Entered STN: 22 Apr 2001
TI Preparation of 19-norsteroids, particularly Δ5(10)-19-norsteroids oxygenated in 6-position
PA CIBA Ltd.
SO 20 pp.
DT Patent
LA Unavailable
IC C07C
CC 42 (Steroids)
FAN.CNT 1

	PATENT NO.	KIND	DATE	APPLICATION NO.	DATE	
PI	FR 1369017		19640807	FR		<--
	GB 1011573			GB		
	NL 295431			NL		
	US 3178419		1965	US		<--
PRAI	CH		19620718	<--		

CLASS

PATENT NO.	CLASS	PATENT FAMILY CLASSIFICATION CODES	
FR 1369017	IC	C07C	
US 3178419	NCL	540/008.000; 540/017.000; 540/023.000; 540/025.000; 540/076.000; 540/105.000; 552/561.000; 552/583.000; 552/586.000; 552/590.000; 552/606.000; 552/607.000; 552/615.000; 552/633.000; 552/636.000; 552/637.000; 552/638.000; 552/639.000; 552/646.000; 552/650.000	<--

OS CASREACT 62:3268
AB The title compds. are prepared from Δ5-19-hydroxysteroids by oxidation with Pb(OAc)4. Acetylation of 8.6 g. 19-hydroxyandrost-4-ene-3,17-dione in 50 ml. Ac2O and 50 ml. C5H5N gave an oily acetate which was refluxed 22 hrs. with 500 ml. C6H6, 50 ml. (CH2OH)2, and 500 mg. TsOH (Ts = tosyl). The mixture was poured on ice and extracted with Et2O, the extract washed with NaHCO3 and evaporated, and the oily residue refluxed 1 hr. with 400 ml. 5% methanolic KOH. Dropwise addition of H2O gave a precipitate, which was taken up in AcOEt and filtered off on Al2O3, then recrystd. from Me2CO-petr. ether to give 6.8 g. 3,3:17,17-bis (ethylenedioxy)-19-hydroxyandrost-5-ene (I), m. 199-200°, [α]D -- 59°. A mixture of 3.25 g. dry Pb(OAc)4 and 3.25 g. CaCO3 was refluxed briefly in 175 ml. absolute C6H6, cooled, refluxed 6 hrs. after addition of 3.25 g. I, and kept overnight at room temperature The resulting oil (3.5 g.), after chromatography on silica gel was saponified with 250 ml. 5% methanolic KOH (1 hr. room temperature) and gave 2.71 g. 3,3:17,17-bis(ethylenedioxy)-6-hydroxy-19-norandrost-5(10)-ene (II), m. 150-2° (Me2CO-petr. ether); after 3 more recrystns. m. 157-8°, [α]D 73°. Similarly prepared was 1 g. 3,3:20,20-bis (ethylenedioxy)-6-hydroxy-19-norpregn-5(10)ene from 1.5 g. 3,3:20,20-bis(ethylenedioxy)-19-hydroxypregn-5-ene. A solution of 2.715 g. II in 46 ml. CHCl3 containing 2.37 g. BzOOH was kept overnight at 4°, diluted with Et2O, and poured on ice. The organic phase was washed with KI, Na2S2O3, H2O, NaHCO3, and H2O and the crude product chromatographed to yield 3,3:17,17-bis(ethylenedioxy)-5,10-oxido-6-hydroxy-19-norandrostane (III) 1.336 g., m. 133° (Me2CO-petr. ether), [α]D 12°. A solution of 245 mg. III in little C5H5N was added dropwise to 250 mg. CrO3 in 1 ml. C5H5N and the mixture kept overnight to give 227 mg. 3,3:17,17-bis (ethylenedioxy)-5,10-oxido-19-norandrostan-6-one (IV), m. 137-8° (2 + Me2CO-petr. ether), [α]D --94°. A mixture of 200 mg. II and 500 mg. (iso-Pr)3Al in 40 ml. absolute C6H6 and 4 ml. Me2CO refluxed 16 hrs. yielded 197 mg. crude product which was dissolved in 9:1 C6H6-Et2O and filtered through Al2O3 to give 160 mg. 3,3:17,17-bis(ethylenedioxy)-19-norandrost-5(10)-en-6-one (V), m. 178-80° (2 + Me2CO-petr. ether), [α]D 43°. A solution of 470 mg. V in 15 ml. AcOH, 15 ml. MeOH, and 7 drops H2O was heated 1 hr. at 60°. The crude reaction product (490 mg.) was filtered in 1:1 C6H6-Et2O through Al2O3 to give 406 mg. 3,3-ethylenedioxy-19-norandrost-5(10)-ene-6,17-dione (VI), m. 189-90° (3 + Me2CO-petr. ether), [α]D 167°. VI

(250 mg.) in 10 ml. AcOH was refluxed 1 hr. and evaporated in vacuo. Chromatography of the residue on Al2O3 gave 136 mg. 19-norandrost-5(10)-ene-3,6,17-trione (VII), m. 163° (3 + Me2CO-petr. ether). A solution of 1 g. V in 10 ml. EtOH, 31 ml. diethylene glycol, and 10 ml. N2H4.H2O was refluxed 1.5 hrs., cooled, and heated again 30 min. at 100° after addition of 5 g. KOH, 60 ml. diethylene glycol was added, EtOH distilled, and the temperature raised to 190°. The mixture was refluxed 3.25 hrs. and the reaction product isolated, and chromatographed on Al2O3 to give 483 mg. 3,3:17,17-bis(ethylenedioxy)19-norandrost-5-ene (VIII), m. 135-7° (2 + Me2CO-petr. ether), [α]D -- 196°.
VIII (40 mg.) was refluxed 1 hr. with 6 ml. AcOH and 10 drops H2O, the solution evaporated in vacuo, and the residue in Et2O filtered through Al2O3 to give 20 mg. product, m. 163-4° (twice, Me2CO-petr. ether) and proved to be identical with 19-norandrost-4-ene-3,17-dione. To a solution of 3 g. Pb(OAc)4 and 2 g. BaCO3 in 150 ml. cyclohexane, heated briefly to boil, was added 2 g. 3β,17β-diacetoxy-19-hydroxyandrost-5-ene, m. 148-9°. The mixture was refluxed 8 hrs. and evaporated in vacuo after removal of the inorg. salts. The residue was dissolved in 100 ml. 3:1 MeOH-H2O and the solution refluxed 2 hrs. with 2 g. K2CO3 to give 1.4 g. crude 3β,6,17β-trihydroxy-19-norandrost-5(10)-ene, which was dissolved in 50 ml. Me2CO and oxidized with 2 ml. 8N CrO3-solution in H2SO4 (1 hr., 0°). Crystallization from Me2CO-petr. ether yielded 980 mg. VII, m. 163°, [α]25D 219°. Similarly, 3β,20β-diacetoxy-19-hydroxy-pregn-5-ene was converted in 50% yield to 19-norpregn-5(10)-ene-3,6,20-trione. Ir and uv data are given.

IT Norsteroids
(19-, 6-oxy Δ5(10)-)

IT Spectra, visible and ultraviolet
(of 5,10-epoxyestrane-3,6,17-trione cyclic 3,17-bis(ethylene acetal) and congeners)

IT 5β-Estrane-3,17-dione, 5,10-epoxy-6-hydroxy-, cyclic bis(ethylene acetal)
5β-Estrane-3,6,17-trione, 5,10-epoxy-, cyclic 3,17-bis(ethylene acetal)

IT 1091-89-0, Estr-5(10)-ene-3,6,17-trione 1240-11-5, Estr-5(10)-ene-3,6,17-trione, cyclic 3-(ethylene acetal) 1243-85-2, Estr-5-ene-3,17-dione, cyclic bis(ethylene acetal) 1246-95-3, Estr-5(10)-ene-3,17-dione, 6-hydroxy-, cyclic bis(ethylene acetal) 1246-96-4, Estr-5(10)-ene-3,6,17-trione, cyclic 3,17-bis(ethylene acetal) 1249-35-0, Androst-5-ene-3,17-dione, 19-hydroxy-, cyclic bis(ethylene acetal) 1249-36-1, Androst-5-ene-3β,17β,19-triol, 3,17-diacetate 1253-50-5, Pregn-5-ene-3,20-dione, 19-hydroxy-, cyclic bis(ethylene acetal)
(preparation of)

IT 546-67-8, Lead acetate, Pb(OAc)4
(reactions of, with 19-hydroxyandrost-5-ene-3,17-dione cyclic bis(ethylene acetal))

IT 166-68-7, Dispiro[1,3-dioxolane-2,3'(4'H)-[5,10]epoxy[17H]cyclopenta[a]phenanthrene-17',2''-[1,3]dioxolane] 187-08-6, Dispiro[1,3-dioxolane-2,3'-[3H]cyclopenta[a]phenanthrene-17'(2'H),2''-[1,3]dioxolane]
(steroid derivs.)

L25 ANSWER 13 OF 15 HCAPLUS COPYRIGHT 2005 ACS on STN
AN 1965:3267 HCAPLUS
DN 62:3267
OREF 62:620g-h,621a-c
ED Entered STN: 22 Apr 2001
TI 11β,12β-Epoxypregnane-3,20-dione
IN Julian, Percy L.; Magnani, Arthur
PA Smith Kline & French Laboratories
SO 8 pp.
DT Patent
LA Unavailable
INCL 260239550
CC 42 (Steroids)
FAN.CNT 1

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE

PI	US 3153646		19641020	US	19570321 <--

CLASS

PATENT NO.	CLASS	PATENT FAMILY CLASSIFICATION CODES
US 3153646	INCL	260239550
US 3153646	NCL	540/082.000; 552/535.000; 552/584.000; 552/587.000; 552/588.000 <--

GI For diagram(s), see printed CA Issue.

AB In addition to the information in Brit. 846,045 (CA 55, 10508g) the following new procedures were described. 11β,12β-Epoxypregnane-3β,20β-diol (I) (2 g.) in 20 cc. C5H5N added to 3 g. CrO3 suspended in 30 cc. C5H5N and the mixture left 16 hrs. gave 1.35 g. 11β,12β-epoxypregnane-3,20-dione (II), m. 142-4° (Me2CO). II (34.3 g.) in 450 cc. Me2CO treated under cooling with 80 cc. 4N HBr gave 40.5 g. 12α-bromopregnan-11β-ol-3,20-dione (III), m. 239-40°. Br (11 g.) in 100 cc. HCONMe2 stirred and heated 15 min. at 45° with 25.6 g. III in 250 cc. HCONMe2 and 400 mg. p-MeC6H4SO3H gave 28 g. 4,12-dibromopregnan-11β-ol-3,20-dione (IV), m. 218-20° (Me2CO). IV (21.8 g.), 175 cc. HCONMe2, and 5.7 g. LiCl heated 3 hrs. at 94-6° under N gave 14.5 g. 12α-bromopregn-4-ene-11β-ol-3,20-dione (V), m. 218-20°. V (2.97 g.), 30 cc. MeOH, 6 cc. H2O, and 1.5 g. K2CO3 refluxed 15 min. gave 11β,12β-epoxypregn-4-ene-3,20-dione, m. 168-70° (Me2CO). Pregn-11-ene-3,20-dione (2 g.) in 50 cc. Et2O left 24 hrs. at 25° with 10% excess monoperphthalic acid in Et2O gave 11α,12α-epoxypregnane-3,20-dione. The allo isomer of I (5 g.), 5 cc. C5H5N, 40 cc. AcOH, and 5 cc. H2O treated in the cold with 4 g. CrO3 in aqueous AcOH, and the mixture left 5 hrs. at room temperature and worked up gave 11β,12β-epoxyallopregnane-3,20-dione. 11β,12β-Epoxypregnan-21-o1-3,20-dione acetate (VI) left overnight with NaOMe-MeOH gave 11β,12β-epoxypregnan-21-o1-3,20-dione (VII). 11β,12β-Epoxypregnan-21-o1-3,20-dione 21-propionate was obtained by treatment of the 11,12-dibromo compound with Na propionate and NaHCO3, followed by oxidation with CrO3 in C5H5N. VII (1 g.) in 25 cc. Me2CO and 0.5 ml. C5H5N left overnight at room temperature with 0.5 g. succinic anhydride gave the hemisuccinate, which treated with Na and Et2O gave the Na salt. VI (5 g.) in dioxane left several hrs. at room temperature with 10 cc. HBr-dioxane gave 12-bromopregnane-11β,21-diol3,20-dione 21-acetate (VIII). VIII (5.3 g.) in HCONMe2 and a trace of p-MeC6H4SO3H with 2.2 g. Br gave 4,12-dibromopregnane-11β,21-diol-3,20-dione 21-acetate (IX). IX (5 g.) in 50 cc. C5H5N was heated to effect dehydrobromination, and 1.5 g. of the product refluxed several hrs. with 25 cc. Me2CO, 3.7 g. KOAc, and 330 mg. NaHCO3 to give 11β,12β-epoxypregn-4-en-21-o1-3,20-dione 21-acetate (X). X (750 mg.) treated with dilute NaOH gave 11β,12β-epoxypregn-4-en-21-o1-3,20-dione.

IT 1099-19-0, 5α-Pregnane-3,20-dione, 11β,12β-epoxy-
1099-20-3, Pregn-4-ene-3,20-dione, 11β,12β-epoxy- 1100-16-9,
5β-Pregnane-3,20-dione, 12α-bromo-11β-hydroxy-
1104-14-9, 5β-Pregnan-20-one, 11β,12β-epoxy-3α,21-dihydroxy-, 21-acetate 1240-91-1, 5β-Pregnane-3,20-dione,
11β,12β-epoxy- 1242-46-2, 5β-Pregnan-20-one,
12α-bromo-3α,11β-dihydroxy- 1242-47-3,
Pregn-4-ene-3,20-dione, 12α-bromo-11β-hydroxy- 1244-45-7,
5β-Pregnane-3,20-dione, 4β,12α-dibromo-11β-hydroxy-
1244-81-1, 5β-Pregnan-20-one, 12α,21-dibromo-3α,11β-dihydroxy- 1249-88-3, 5β-Pregnane-3,20-dione, 11β,12β-epoxy-21-hydroxy-, acetate
(preparation of)

L25 ANSWER 14 OF 15 HCAPLUS COPYRIGHT 2005 ACS on STN
AN 1963:448604 HCAPLUS
DN 59:48604
OREF 59:8825e-h,8826a-h,8827a-b
ED Entered STN: 22 Apr 2001
TI Reduction of 10-cyano-Δ5-steroids by means of alkali metal solutions

AU Gardi, Rinaldo; Pedrali, Cesare; Ercoli, Alberto
SO Gazzetta Chimica Italiana (1963), 93(5), 525-41
CODEN: GCITA9; ISSN: 0016-5603
DT Journal
LA Unavailable
CC 42 (Steroids)
GI For diagram(s), see printed CA Issue.
AB To a solution of 2.1 g. 10-cyano-19-nor-5-androstene-3β,17β-diol (I) in 380 ml. Me2CO was added dropwise under N 5 ml. 8N chromic acid. After 5 min. stirring (under N) the mixture was poured into H2O and extracted with Et2O. From the Et2O exts. was obtained 1.35 g. 10-cyano-19-nor-5-androstene-3,17-dione (II), m. 152-6° (MeOH), [α]D -69°. To a solution of 840 mg. II in 75 ml. C6H6 was added 3 ml. ethylene glycol containing 50 mg. p-toluenesulfonic acid. The mixture was refluxed overnight, and H2O separated from the reaction by a Marcusson separator. A few drops of pyridine was added and most of the C6H6 was taken off in vacuo. The residue, taken up in MeOH, crystallized to give 785 mg. 10-cyano-19-nor-5-androstene-3,17-dione bis(ethylene ketal) (III), m. 211-12° (MeOH), [α]D -133° (dioxane). To a suspension of 10 g. Na in 150 ml. refluxing dry toluene was added a solution of 1.1 g. III in a mixture of 15 ml. EtOH and 15 ml. dry toluene, 40 ml. more dry EtOH added, the mixture cooled, the Na decomposed with EtOH, and the mixture diluted with H2O. The toluene was separated and the aqueous layer extracted with Et2O. From the combined organic exts. was obtained 1 g. gummy 3,3,17,17-bis(ethylenedioxy)-19-norandrostene [Δ5(10) + Δ5] (IV), [α]D 35°. Likewise a mixture of 7.2 g. 19-nor-4-androstene-3,17-dione (V), 500 mg. p-toluenesulfonic acid, and 30 ml. ethylene glycol in 560 ml. C6H6 was treated as described for the preparation of III. Here 5.95 g. gummy IV was obtained. IV was also obtained by similarly preparing the diketal (VI) of 19-nor-5(10)-androstene-3,17-dione (VII, Δ5(10)). To a solution of 2 g. IV in 200 ml. Et2O was added 20 ml. 15% Et2O solution of monoperphthalic acid. The next day the Et2O was washed with NaHCO3, then H2O. A gum (1.99 g.) was obtained, which was taken up in C6H6 and chromatographed (Florisil). From C6H6-Et2O (3:2) was obtained 1.3.5 g. crude material. Recrystns. from MeOH, then hexane, gave 5β,10β-oxido-19-norandrostane-3,17-dione 3,17-bis(ethylene ketal) (VIIa), m. 116-17°, fold 10°. Evaporation of the MeOH liquors from the above and recrystn. (MeOH) gave 98 mg. 5α,10α-oxido-19-norandrostane-3,17-dione 3,17-bis(ethylene ketal) (VIII), m. 120-1°, [α]D 20°. The last column elution (C6H6:Et2O, 1:1) gave 370 mg. 5α,6α-oxido-19-norandrostane-3,17-dione 3,17-bis(ethylene ketal) (IX), m. 190-1° (MeOH), [α]D -41°. A solution of 500 mg. VIIa in 20 ml. 50% HOAc was left 15 hrs. at room temperature After dilution in H2O and salting with NaCl, the mixture was extracted with CHCl3. From this extract was obtained 320 mg. 19-norandrostane-5α,10β-diol-3,17-dione (X), m. 240-1° (Me2CO-hexane), [α]D 97°. Likewise treatment of IX in the same manner gave X. A solution of 100 mg. X in 5 ml. Me2CO, treated with dilute HCl, was refluxed 20 min. After evaporation of solvent, the residue was taken up in Et2O. Repeated recrystns. (Me2CO-hexane) gave 19-nor-4-androsten-10β-ol-3,17-dione (XI), m. 206-7°, [α]D 148°. XI was also obtained by treating VIIa and VIII with dilute HCl. A solution of 100 mg. XI in 5 ml. Me2CO was refluxed 30 min. with concentrated HCl. Dilution with H2O gave 66 mg. estrone (XII), m. 250-3°, [α]D 163° (dioxane). To a suspension of 10 g. Na in 100 ml. dry boiling toluene was added 1.25 g. I, dissolved in 35 ml. absolute EtOH. The reaction was run as in the preparation of IV to give 1.05 g. 19-nor-androstene-3β,17β-diol (mixture of isomers) (XIII), m. 148-51° (Me2CO), [α]D 73°. XIII (100 mg.) was treated with Ac2O in pyridine. The diacetate (XIV) formed, m. 82-4° (MeOH), [α]D 32°. A solution of 1.59 g. I in 30 ml. tetrahydrofuran and 30 ml. absolute EtOH was added dropwise to 300 ml. liquid NH3. Li was added portionwise to the persistence of a blue color and the mixture stirred until the blue disappeared. To this was added 50 ml. EtOH and most of the solvent removed. When the volume was approx. 100 ml., 200 ml. Et2O was added and the mixture heated to rid of NH3. After dilution with

H2O, and washing and drying the organic extract, evaporation gave 1.22 g. XIII, m. 148-50° (Me2CO), [α]D 55°. To a solution of 275 mg. of the diol mixture XIII in 75 ml. CHCl3 was added 160 mg. Br in CHCl3. After evaporation of CHCl3 the residue was dissolved in 15 ml. AcOH and treated overnight with 300 mg. CrO3 in 3 ml. HOAc. This was poured into H2O, extracted with Et2O and the solid residue obtained was dissolved in 43 ml. EtOH and refluxed 3 hrs. with 600 mg. Zn. Removal of Zn and evaporation of EtOH gave a semi-oil residue mixture of VII. Recrystn. (MeOH-then aqueous MeOH) gave VII, m. 141-3°, [α]D 268°. A solution of 500 mg. XIII in 160 ml. Me2CO was oxidized with 8N CrO8 (as in preparation of II). A residue (280 mg.) was worked up with Et2O to give 35 mg. VII [Δ5(10)], which on crystallization m. 142-4°, [α]D 268°.

To a solution of 500 mg. of the diol mixture XIII in 30 ml. toluene and 6 ml. cyclohexane was added 550 mg. Al(OPr-iso)3 in 10 ml. dry toluene and the mixture refluxed 3 hrs. Addition of aqueous HCl caused separation of phases. The aqueous phase was extracted with Et2O and the Et2O and toluene combined. After washing the combined organic phase with H2O, the mixture was steam distilled The residue, extracted again with Et2O, gave 300 mg. oily mixture of V and 19-nor-5(10)-androstene-3,17-dione (VII, Δ5(10)). A solution of 100 mg. of the mixture VII, in 8 ml. MeOH was treated with 5 drops 2N KOH 15 min. under N. Evaporation in vacuo and dilution with H2O gave 72 mg. V, which on recrystn. (MeOH), m. 168-70°, [α]D 136°. To a solution of the ketal IV, obtained by reduction of 640 mg. III, in 40 ml. MeOH was added dilute HCl and the mixture refluxed 15 min. Dilution with H2O gave 266 mg. V, m. 168-70° (MeOH), [α]D 136°. One g. 10-cyano-19-nor-5-pregnene-3β,20β-diol (XV) was oxidized with CrO3 (as in the preparation of II). Here 645 mg. 10-cyano-19-nor-5-pregnene-3,20-dione (XVI) was obtained, which on recrystn. (MeOH) m. 192-6°, [α]D -45°. Next 4 g. XVI was treated with ethylene glycol in C6H6 and p-toluenesulfonic acid to give 3.95 g. 10-cyano-19-nor-5-pregnene-3,20-dione bis(ethylene ketal) (XVII), m. 209-10° (CH2Cl2MeOH), [α]D -82° (dioxane). A MeOH solution of 200 mg. XVII was heated 15 min. with a few drops dilute HCl to give 10-cyanonorprogesterone (XVIII), m. 159-61° (MeOH), [α]D 263°. From 1.1 g. XVII by reduction with Na-EtOH in toluene, there was obtained 725 mg. 3,3,20,20-bis(ethylenedioxy)-19-nor-5(10)pregnene (XIX), m. 140-1°, [α]D 108° (dioxane). A solution of 900 mg. XVII in 20 ml. dry tetrahydrofuran and 200 ml. absolute EtOH was added to 200 ml. liquid NH3, then treated with Li (as in the preparation of XIII). This gave 609 mg. XIX, m. 140-1° (MeOH), [α]D 107°. 19-Norprogesterone (XX) was treated with ethylene glycol in the usual manner to give 1.1 g. XIX, m. 137-8°, [α]D 108° (dioxane). To a solution of 250 mg. XIX in 20 ml. Et2O was added 6 ml. 18% Et2O solution of monoperphthalic acid and the mixture left overnight. From the Et2O after workup was obtained 225 mg. 5β,10β-oxido-19-norpregnane-3,20-dione 3,20-bis(ethylene ketal) (XXI), m. 129-32°, chromatographed on Florisil. From the C6H6-Et2O (3:2) eluate was obtained 205 mg. pure XXI, m. 136-7° (MeOH), [α]D 58°. Reduction of 1.25 g. XV with Na-EtOH in toluene gave 965 mg. 19-norpregnene-3β,20β-diol (mixture of isomers) (XXII), m. 160-2° (Me2CO), [α]D 70°. XXII (200 mg.) was acetylated with Ac2O in pyridine to give 194 mg. 19-norpregnene-3β,20β-diol diacetate (XXIII), m. 108-10° (MeOH), [α]D 74°. Reduction of 1.6 g. XV with Li-EtOH in NH3 gave 1.35 g. of the mixture XXII, m. 159-62°, [α]D 68°.

XXII was oxidized as was XIII. From 900 mg. XXII after bromination, CrO3 oxidation, and debromination with Zn, was obtained 305 mg. of a mixture of diones, m. 62-5°. After digestion in Et2O-petr. ether, 110 mg. 19-nor-5(10)-pregnene-3,20-dione (XXIV) was obtained which on recrystn. (dilute MeOH) gave pure XXIV, m. 101-2°, [α]D 246°.

From the oxidation of 500 mg. XXII with 8N CrO3 was obtained 290 mg. gum, which yielded (Et2O-petr. ether) 35 mg. XXIV, m. 98-101°.

Oppenauer oxidation of 500 mg. XXII gave 285 mg. oily product, consisting of a mixture of 19-norpregnene-3,20-dione isomers. XXIV was also isolated following mild hydrolysis of XIX. A suspension of 100 mg. XIX in 8 ml. 50% HOAc was shaken and left overnight. After H2O dilution and Et2O extraction,

work up yielded an oil, which on treatment with aqueous MeOH gave 40 mg. XXIV, m. 101-2° (MeOH). A solution of 100 mg. XXIV was treated with 2N KOH to give 85 mg. XX, m. 144-5° (MeOH), [α]D 147°. The diketal (XIX) (650 mg.) hydrolyzed by slight warming in MeOH-dilute HCl gave 430 mg. XX, m. 141-3°, which on recrystn. (MeOH) gave anal. pure XX identical with the product prepared by other methods.

IT Spectra, visible and ultraviolet
(of estr-4-ene-3,17-dione and congeners)

IT Reduction
Spectra, infrared
(of Δ5-steroid 19-nitriles)

IT Steroids
(Δ5-unsatd., 19-nitriles, reduction of)

IT 19-Norpregn-5(10)-ene-3β,20β-diol, diacetate, mixture with Δ5 analog
19-Norpregn-5(10)-ene-3β,20β-diol, mixture with Δ5 analog
19-Norpregn-5-ene-3β,20β-diol, diacetate, mixture with Δ5(10) analog
19-Norpregn-5-ene-3β,20β-diol, mixture with Δ5(10) analog
5α-Estrae-3,17-dione, 5,10-dihydroxy-
5α-Estrae-3,17-dione, 5,6α-epoxy-, cyclic bis(ethylene acetal)
Estr-5(10)-ene-3,17-dione, cyclic bis(ethylene acetal), mixture with Δ5 analog
Estr-5(10)-ene-3β,17β-diol, diacetate, mixture with Δ5 analog
Estr-5(10)-ene-3β,17β-diol, mixture with Δ5 analog
Estr-5-ene-3,17-dione, cyclic bis(ethylene acetal), mixture with Δ5(10) analog
Estr-5-ene-3β,17β-diol, diacetate, mixture with Δ5(10) analog
Estr-5-ene-3β,17β-diol, mixture with Δ5(10) analog

IT 53-16-7, Estrone 472-54-8, 19-Norpregn-4-ene-3,20-dione 734-32-7, Estr-4-ene-3,17-dione 1038-51-3, 19-Norpregn-5(10)-ene-3,20-dione **1624-60-8**, 5β-Estrane-3,17-dione, 5,10-epoxy-, cyclic bis(ethylene acetal) 1624-72-2, 19-Nor-5β-pregnane-3,20-dione, 5,10-epoxy-, cyclic bis(ethylene acetal) 3962-66-1, Estr-5(10)-ene-3,17-dione 5772-67-8, Androst-5-ene-19-nitrile, 3,17-dioxo-, cyclic bis(ethylene acetal) 95289-85-3, Pregn-4-ene-19-nitrile, 3,20-dioxo- 95289-86-4, Pregn-5-ene-19-nitrile, 3,20-dioxo- 101298-83-3, 19-Norpregn-5(10)-ene-3,20-dione, cyclic bis(ethylene acetal) 102049-34-3, Pregn-5-ene-19-nitrile, 3,20-dioxo-, cyclic bis(ethylene acetal) **102490-33-5**, 5α,10α-Estrane-3,17-dione, 5,10-epoxy-, cyclic bis(ethylene acetal)
(preparation of)

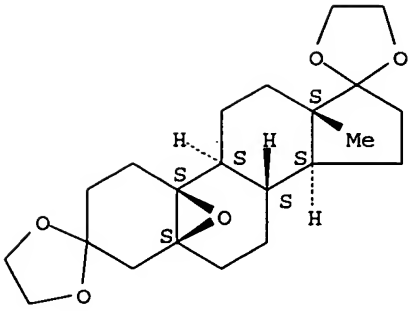
IT 166-68-7, Dispiro[1,3-dioxolane-2,3'(4'H)-[5,10]epoxy[17H]cyclopenta[a]phenanthrene-17',2''-[1,3]dioxolane] 175-26-8, Dispiro[1,3-dioxolane-2,3'(4'H)-[5,6]epoxy[5H]cyclopenta[a]phenanthrene-17'(2'H),2''-[1,3]dioxolane] 187-08-6, Dispiro[1,3-dioxolane-2,3'-[3H]cyclopenta[a]phenanthrene-17'(2'H),2''-[1,3]dioxolane]
(steroid derivs.)

IT **1624-60-8**, 5β-Estrane-3,17-dione, 5,10-epoxy-, cyclic bis(ethylene acetal) **102490-33-5**, 5α,10α-Estrane-3,17-dione, 5,10-epoxy-, cyclic bis(ethylene acetal)
(preparation of)

RN 1624-60-8 HCAPLUS

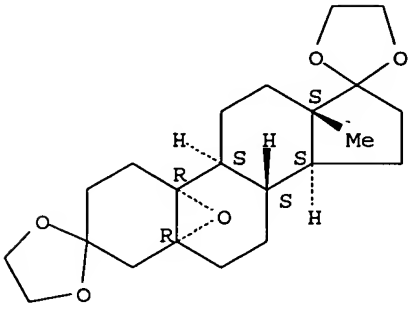
CN Estrane-3,17-dione, 5,10-epoxy-, cyclic bis(1,2-ethanediyl acetal), (5β)- (9CI) (CA INDEX NAME)

Absolute stereochemistry.



RN 102490-33-5 HCAPLUS
CN Estrane-3,17-dione, 5,10-epoxy-, cyclic bis(1,2-ethanediyl acetal), (5α,10α)- (9CI) (CA INDEX NAME)

Absolute stereochemistry.



L25 ANSWER 15 OF 15 HCAPLUS COPYRIGHT 2005 ACS on STN
AN 1963:448603 HCAPLUS
DN 59:48603
OREF 59:8824g-h,8825a-e
ED Entered STN: 22 Apr 2001
TI Synthesis of pregnanediol derivatives. IV. Synthesis of Bhomo-5α-pregnane-3α,20α-diol
AU Himizu, Junichi
CS Tanabe Seiyaku Co., Saitama, Japan
SO Yakugaku Zasshi (1963), 83, 620-3
CODEN: YKKZAJ; ISSN: 0031-6903
DT Journal
LA Unavailable
CC 42 (Steroids)
AB cf. CA 59, 3985f. 3β-Acetoxycholestan-6-one (0.5 g.) in 10 ml. EtOH and 1 g. KCN at 0° treated dropwise with 2 ml. AcOH and the product extracted with Et2O gave the 6-cyanohydrin, oil, catalytic reduction of which in 10 ml. AcOH over 0.15 g. PtO2 absorbed 2.3 moles H; the solution treated with 100 ml. H2O, kept overnight, the precipitate filtered off, the filtrate containing the 6-amino alc. acetate compound cooled; and this treated in H2O with HNO2 gave 19 mg. 3β-acetoxy-B-homocholestan-7-one (I), m. 118-20°; semicarbazone m. 197° (decomposition); benzoate m. 152°. 3βAcetoxycholestan-7-one (2 g.) in 20 ml. acetone cyanohydrin treated with 1 drop 10% NaOH, kept 10 min., H2O added, and the product filtered off gave 2.1 g. 7-cyanohydrin compound; catalytic reduction of this in 50 ml. AcOH over 0.3 g. PtO2, treating the solution with 150 ml. H2O containing 2 g. NaNO2, keeping overnight, and chromatographing the product (Al2O3) gave 0.7 g. I, m. 118-20°. Pregn-5-ene-3β,20α-diol diacetate (3.2 g.) in 15 ml. CCl4, 4 ml. Ac2O, and 8 ml. AcOH at 80° treated dropwise with CrO3-tert-BuOH (4 g. CrO3), the mixture stirred 9 hrs. at

80°, cooled, poured into a cooled solution of 10 g. (CO2H)2 in 500 ml. H2O, the whole kept overnight, and the product extracted with CHCl3 gave 1.7 g. 3β,20α-diacetoxypregn-5-en-7-one (II), m. 163-4°, [α]24D 121.4°. Catalytic reduction of 9 g. II in 100 ml. AcOEt over 5 g. 5% Pd-C gave 6.3 g. 3β,20α-diacetoxy-5α-pregnan-7-one (III), m. 186-7° (MeOH), [α]24D -46.2°. III (2 g.) in 60 ml. MeOH, 5 ml. H2O, and 0.3 g. K2CO3 refluxed 30 min., cold H2O added, the product extracted with Et2O and chromatographed on Al2O3 (3:7 hexane-C6H6) gave 1 g. 3β-hydroxy-20α-acetoxy-5α-pregnan-7-one (IV), m. 160-1.5°; IV and p-MeC6H4SO2Cl gave the 3β-tosyloxy analog of IV, m. 153-4°, [α]24D -34.7°. A mixture of 1 g. above tosylate, 15 ml. AcOH, 3 ml. Ac2O, and 3 g. KOAc refluxed 3 hrs., the product extracted with Et2O and chromatographed on Al2O3 in 7:3 hexane-C6H6 gave 0.3 g. 20α-acetoxy-5α-pregnen-2(or 3)-en-7-one (V), and the 4:6 hexane-C6H6 effluent gave 0.15 g. 3α,20α-diacetoxy-5α-pregnan-7-one (VI), m. 154° (MeOH). II (0.2 g.) in 15 ml. MeOH and 2.5 ml. concentrated HCl refluxed 3 hrs. and the product extracted with Et2O gave 20α-acetoxypregna-3,5-dien-7-one (VII), m. 111-11.5°. Catalytic reduction of 30 mg. VII in 1.5 ml. AcOH over 10 mg. PtO2 and keeping the product overnight in a mixture of 2 ml. 80% AcOH and 10 mg. CrO3 gave 12 mg. 20α-acetoxy-5α-pregnan-7-one (VIII), m. 130-1°. Also, catalytic reduction of 0.3 g. VII in 7 ml. AcOH over 0.1 g. PtO2 and oxidation of the product with AcOH-CrO3 gave 1.6 g. VIII, m. 130-1°. VI (0.2 g.) in 3 ml. Me2CO cyanohydrin treated with 1 drop 10% NaOH, the mixture kept 10 min., H2O added, and the product extracted with Et2O gave an oily substance; catalytic reduction of this in 6 ml. AcOH over 30 mg. PtO2, treating the product with 25 ml. H2O, the solution at -5° treated with 0.2 g. NaNO2 in 3 ml. H2O, kept overnight at room temperature, and the product filtered off and chromatographed (Al2O3) with hexane-C6H6 gave 70 mg. 3α,20α-diacetoxy-B-homo-5α-pregnan-7-one (IX), m. 194-5° (MeOH). IX (50 mg.) in 2 ml. EtSH at 0° treated with 70 mg. ZnCl2 and 150 mg. Na2SO4, kept 2 days at 5°, the EtSH removed in vacuo, the residue with H2O extracted with Et2O gave a thioketal, oil; catalytic reduction of this in dioxane over Raney Ni by heating 15 hrs. on a water bath and concentration of the solution gave 34 mg. of a diacetate, m. 138°, hydrolysis of which KOH-MeOH gave 25 mg. of B-homo-5α-pregnane-3α,20α-diol, m. 194-5°. III (0.5 g.) treated as in IX gave 0.18 g. 3β,20α-diacetoxy-B-homo-5α-pregnan-7-one, m. 149-50° (Me2CO). Similarly, VIII gave 20α-acetoxy-B-homo-5α-pregnan-7-one, m. 132-4°.

IT Spectra, infrared
(of B-homo-5α-pregnane-3α,20α-diol and intermediates)

IT 26445-07-8, Pregnanediol
(derivs.)

IT 1612-79-9, B-Homo-5α-pregnane-3α,20α-diol 1624-76-6, Pregn-5-en-7-one, 3β,20α-dihydroxy-, diacetate 1625-14-5, 5α-Pregnan-7-one, 3β,20α-dihydroxy-, 20-acetate 3-p-toluenesulfonate 1805-05-6, B-Homo-5α-pregnane-3α,20α-diol, diacetate 1805-20-5, 5α-Pregnan-7-one, 3β,20α-dihydroxy-, diacetate 1805-21-6, 5α-Pregnan-7-one, 3α,20α-dihydroxy-, diacetate 1969-99-9, B-Homo-5α-pregnan-7-one, 3α,20α-dihydroxy-, diacetate 2319-65-5, 5α-Pregnan-7-one, 3β,20α-dihydroxy-, 20-acetate 14652-41-6, B-Homo-5α-cholestan-7-one, 3β-hydroxy-, acetate 94914-22-4, Androst-5-ene-19-nitrile, 3,17-dioxo- 95563-87-4, Pregna-3,5-dien-7-one, 20α-hydroxy-, acetate 95565-55-2, 5α-Pregnan-7-one, 20α-hydroxy-, acetate 96811-34-6, 5α-Pregn-2-en-7-one, 20α-hydroxy-(?), acetate 96811-36-8, 5α-Pregn-3-en-7-one, 20α-hydroxy-(?), acetate 101517-16-2, B-Homo-5α-pregnan-7-one, 20α-hydroxy-, acetate 103308-56-1, B-Homo-5α-pregnan-7-one, 3β,20α-dihydroxy-, diacetate 105819-25-8, B-Homo-5α-cholestan-7-one, 3β-hydroxy-, benzoate 108042-16-6, B-Homo-5α-cholestan-7-one, 3β-hydroxy-, semicarbazone, acetate
(preparation of)

```
=> b hcao
FILE 'HCAOLD' ENTERED AT 08:28:52 ON 27 JUN 2005
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FILE COVERS 1907-1966
FILE LAST UPDATED:  01 May 1997 (19970501/UP)

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more information.

=> d all l20 tot

L20  ANSWER 1 OF 3  HCAOLD  COPYRIGHT 2005 ACS on STN
AN   CA63:655g  CAOLD
TI   phenolic steroids and their ethers
AU   Ercoli, Alberto; Gardi, R.; Pedrali, C.
PA   Vismara, Francesco, Societa per Azioni
DT   Patent
     PATENT NO.     KIND          DATE
     ------------   -----------   ----
PI   BE 641351
     DE 1223379
     FR 1394051
     NL 302028
     US 3231567                   1966
IT     72-33-3     152-43-2     858-98-0    1474-50-6    1624-56-2
     1624-60-8    1624-61-9    1624-62-0    1624-63-1    1624-64-2
     1624-66-4    1624-67-5    1624-69-7    1624-70-0    1624-72-2    1624-73-3
     1624-74-4    1624-98-2    1667-98-7    1805-17-0    1852-81-9
     102490-33-5

L20  ANSWER 2 OF 3  HCAOLD  COPYRIGHT 2005 ACS on STN
AN   CA62:621c  CAOLD
TI   19-norsteroids, particularly Δ5(10)-19-norsteroids oxygenated in the
     6-position
PA   CIBA Ltd.
DT   Patent
     PATENT NO.     KIND          DATE
     ------------   -----------   ----
PI   FR 1369017
     GB 1011573
     NL 295431
     US 3178419                   1965
IT     930-66-5    1091-89-0    1103-94-2    1240-11-5    1243-85-2
     1246-95-3    1246-96-4    1249-35-0    1249-36-1    1249-41-8
     1253-50-5

L20  ANSWER 3 OF 3  HCAOLD  COPYRIGHT 2005 ACS on STN
AN   CA59:8825e  CAOLD
TI   reduction of 10-cyano-Δ5-steroids by alkali metal solns.
AU   Gardi, Rinaldo; Pedrali, C.; Ercoli, A.
```

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IT   1038-51-3   1243-85-2   1624-60-8   1624-61-9   1624-72-2
     2220-74-8   3962-66-1   4993-32-2   5189-96-8   5772-67-8  14413-21-9
     21513-92-8  24428-62-4  25975-59-1  31321-37-6  94003-72-2  94914-22-4
     95289-85-3  95289-86-4 101298-82-2 101298-83-3 101517-16-2 102049-34-3
     102490-33-5 103004-85-9 103308-56-1


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STRUCTURE FILE UPDATES:   26 JUN 2005  HIGHEST RN 852987-17-8
DICTIONARY FILE UPDATES:  26 JUN 2005  HIGHEST RN 852987-17-8

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**********************************************************************
*                                                                    *
* The CA roles and document type information have been removed from *
* the IDE default display format and the ED field has been added,    *
* effective March 20, 2005.  A new display format, IDERL, is now     *
* available and contains the CA role and document type information. *
*                                                                    *
**********************************************************************

Crossover limits have been increased.  See HELP CROSSOVER for details.

Experimental and calculated property data are now available. For more
information enter HELP PROP at an arrow prompt in the file or refer
to the file summary sheet on the web at:
http://www.cas.org/ONLINE/DBSS/registryss.html

=> d ide l28 tot

L28  ANSWER 1 OF 4  REGISTRY  COPYRIGHT 2005 ACS on STN
RN   102490-33-5  REGISTRY
ED   Entered STN:  31 May 1986
CN   Estrane-3,17-dione, 5,10-epoxy-, cyclic bis(1,2-ethanediyl acetal),
     (5α,10α)- (9CI)  (CA INDEX NAME)
OTHER CA INDEX NAMES:
CN   5α,10α-Estrane-3,17-dione, 5,10-epoxy-, cyclic bis(ethylene
     acetal) (7CI)
CN   Dispiro[1,3-dioxolane-2,3'(4'H)-[5,10]epoxy[17H]cyclopenta[a]phenanthrene-
     17',2''-[1,3]dioxolane], estrane-3,17-dione deriv.
FS   STEREOSEARCH
MF   C22 H32 O5
SR   CAOLD
LC   STN Files:   BEILSTEIN*, CA, CAOLD, CAPLUS, CASREACT, TOXCENTER, USPATFULL
         (*File contains numerically searchable property data)

Absolute stereochemistry.
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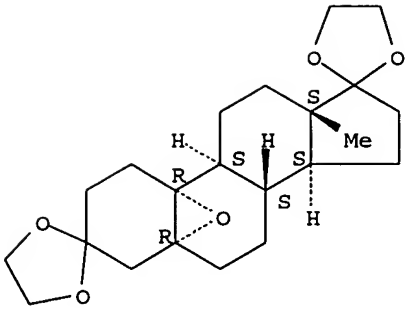
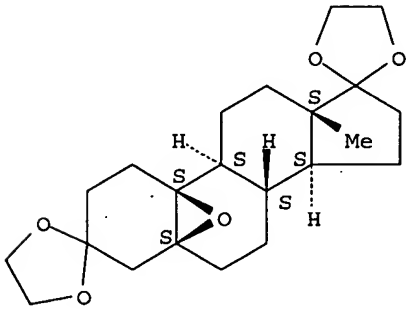


PROPERTY DATA AVAILABLE IN THE 'PROP' FORMAT

6 REFERENCES IN FILE CA (1907 TO DATE)
6 REFERENCES IN FILE CAPLUS (1907 TO DATE)
2 REFERENCES IN FILE CAOLD (PRIOR TO 1967)

L28 ANSWER 2 OF 4 REGISTRY COPYRIGHT 2005 ACS on STN
RN 1624-60-8 REGISTRY
ED Entered STN: 16 Nov 1984
CN Estrane-3,17-dione, 5,10-epoxy-, cyclic bis(1,2-ethanediyl acetal), (5β)- (9CI) (CA INDEX NAME)
OTHER CA INDEX NAMES:
CN 5β-Estrane-3,17-dione, 5,10-epoxy-, cyclic bis(ethylene acetal) (7CI)
CN Dispiro[1,3-dioxolane-2,3'(4'H)-[5,10]epoxy[17H]cyclopenta[a]phenanthrene-17',2''-[1,3]dioxolane], estrane-3,17-dione deriv.
FS STEREOSEARCH
MF C22 H32 O5
LC STN Files: BEILSTEIN*, CA, CAOLD, CAPLUS
(*File contains numerically searchable property data)

Absolute stereochemistry.



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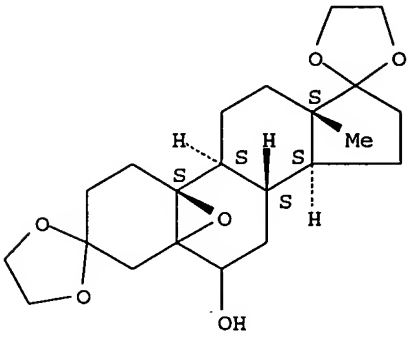
2 REFERENCES IN FILE CA (1907 TO DATE)
2 REFERENCES IN FILE CAPLUS (1907 TO DATE)
2 REFERENCES IN FILE CAOLD (PRIOR TO 1967)

L28 ANSWER 3 OF 4 REGISTRY COPYRIGHT 2005 ACS on STN
RN 1249-41-8 REGISTRY
ED Entered STN: 16 Nov 1984
CN Estrane-3,17-dione, 5,10-epoxy-6-hydroxy-, cyclic bis(1,2-ethanediyl acetal) (9CI) (CA INDEX NAME)
OTHER CA INDEX NAMES:
CN Dispiro[1,3-dioxolane-2,3'(4'H)-[5,10]epoxy[17H]cyclopenta[a]phenanthrene-

17',2''-[1,3]dioxolane], estrane-3,17-dione deriv.
CN Estrane-3,17-dione, 5,10-epoxy-6-hydroxy-, cyclic bis(ethylene acetal) (7CI, 8CI)
FS STEREOSEARCH
MF C22 H32 O6
LC STN Files: BEILSTEIN*, CAOLD
(*File contains numerically searchable property data)

Absolute stereochemistry.



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1 REFERENCES IN FILE CAOLD (PRIOR TO 1967)

L28 ANSWER 4 OF 4 REGISTRY COPYRIGHT 2005 ACS on STN
RN 1103-94-2 REGISTRY
ED Entered STN: 16 Nov 1984
CN Estrane-3,6,17-trione, 5,10-epoxy-, cyclic 3,17-bis(1,2-ethanediyl acetal), (5β)- (9CI) (CA INDEX NAME)
OTHER CA INDEX NAMES:
CN Dispiro[1,3-dioxolane-2,3'(4'H)-[5,10]epoxy[17H]cyclopenta[a]phenanthrene-17',2''-[1,3]dioxolane], estrane-3,6,17-trione deriv.
CN Estrane-3,6,17-trione, 5,10-epoxy-, cyclic 3,17-bis(ethylene acetal) (7CI)
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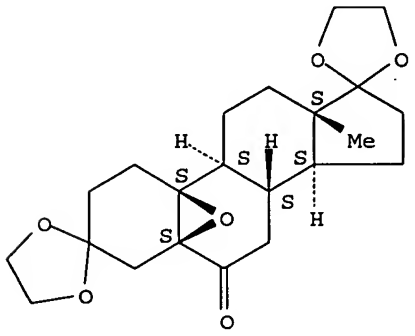
MF C22 H30 O6
LC STN Files: BEILSTEIN*, CA, CAOLD, CAPLUS
(*File contains numerically searchable property data)

Absolute stereochemistry.



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2 REFERENCES IN FILE CA (1907 TO DATE)
2 REFERENCES IN FILE CAPLUS (1907 TO DATE)

Search done by Noble Jarrell

1 REFERENCES IN FILE CAOLD (PRIOR TO 1967)

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L30           0 L29
L31           1 L29 FULL

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FILE CONTENT:1840 - 26 Jun 2005 VOL 142 ISS 26

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**************************************************************
*                                                            *
*     CASREACT now has more than 9.2 million reactions       *
*                                                            *
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This file contains CAS Registry Numbers for easy and accurate substance
identification.

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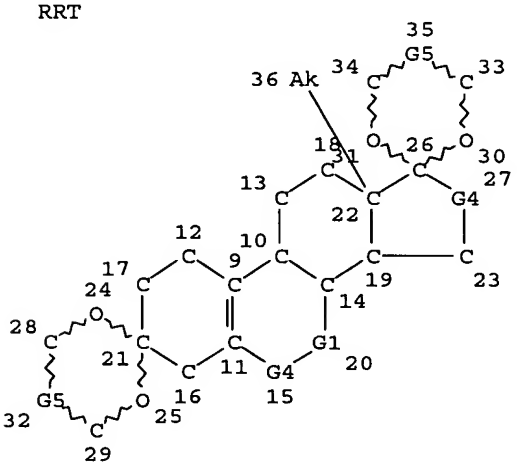
RRT



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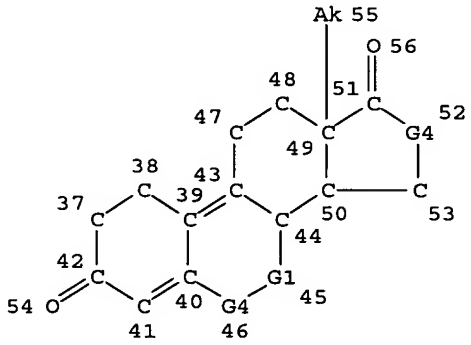

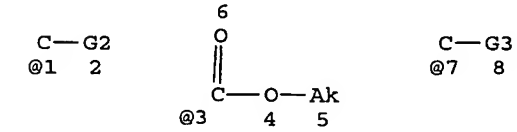


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DEFAULT ECLEVEL IS LIMITED

GRAPH ATTRIBUTES:
RING(S) ARE ISOLATED OR EMBEDDED
NUMBER OF NODES IS  56

STEREO ATTRIBUTES: NONE
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100.0% DONE     18 VERIFIED       3 HIT RXNS                      1 DOCS
SEARCH TIME: 00.00.01


=> d bib abs crd retable l31 tot


L31  ANSWER 1 OF 1  CASREACT  COPYRIGHT 2005 ACS on STN
AN   138:24878  CASREACT
TI   Process for preparing estra-4,9(10)-diene-3,17-dione steroids from
     19-nor-androst-4-ene-3-one steroids
IN   Van Rheenen, Verlan H.; Hessler, Edward J.
PA   Bridge Organics Co., USA
SO   PCT Int. Appl., 23 pp.
     CODEN: PIXXD2
DT   Patent
LA   English
FAN.CNT 1
     PATENT NO.        KIND  DATE           APPLICATION NO.  DATE
     ---------------   ----  --------       ---------------  --------
PI   WO 2002101014      A2   20021219       WO 2002-US18305  20020607
     WO 2002101014      A3   20040325
     WO 2002101014      B1   20040506
         W:  AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN,
             CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH,
             GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR,
             LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, OM, PH,
             PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TN, TR, TT, TZ,
             UA, UG, UZ, VN, YU, ZA, ZM, ZW
         RW: GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW, AM, AZ, BY,
             KG, KZ, MD, RU, TJ, TM, AT, BE, CH, CY, DE, DK, ES, FI, FR, GB,
             GR, IE, IT, LU, MC, NL, PT, SE, TR, BF, BJ, CF, CG, CI, CM, GA,
             GN, GQ, GW, ML, MR, NE, SN, TD, TG
     US 2003004333      A1   20030102       US 2002-163727   20020606
     US 6812358         B2   20041102
     US 2004087785      A1   20040506       US 2003-695122   20031028
PRAI US 2001-296999P   20010608
     US 2002-163727    20020606
OS   MARPAT 138:24878
GI
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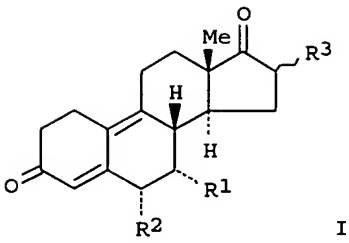

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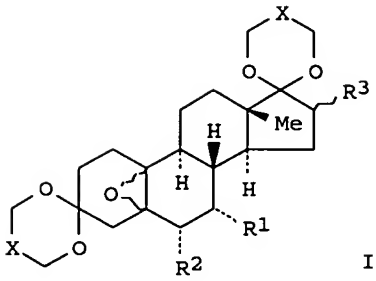
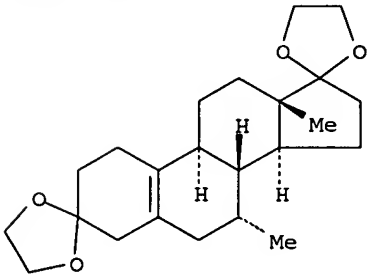


II

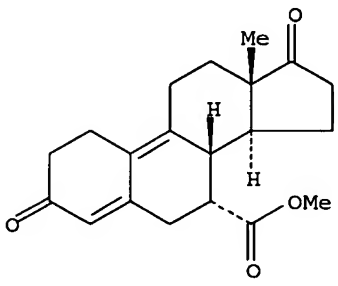
AB The present invention discloses a novel process for preparing estra-4,9(10)-diene-3,17-dione derivs. such as I [R1 = Me, H, CO2Me; R2 = Me, F, H; R3 = Me, OH, F, H], from readily available 19-nor-androst-4-ene-3-one derivs. such as II [X = bond, C(Me)2, CH2], by a three-step process. Thus, epoxidn. of 7α-methyl-estra-5(10)-ene-3,17-dione-3,17-bis-ethylene glycol ketal afforded 7α-methyl-estra-5(10)-oxido-3,17-dione-3,17-bis-ethylene glycol ketal which upon treatment with hydrochloric acid provided 10-hydroxy-7α-methyl-estra-4-ene-3,17-dione (III) and 5,10-dihydroxy-7α-methyl-estra-4-ene-3,17-dione (IV). III and IV were reacted with concentrated sulfuric acid to afford estra-4,9(10)-diene-3,17-dione I [R1 = Me; R2, R3 = H]. Products of this process are important intermediates in the preparation of biol. active substances.

RX(6) OF 17

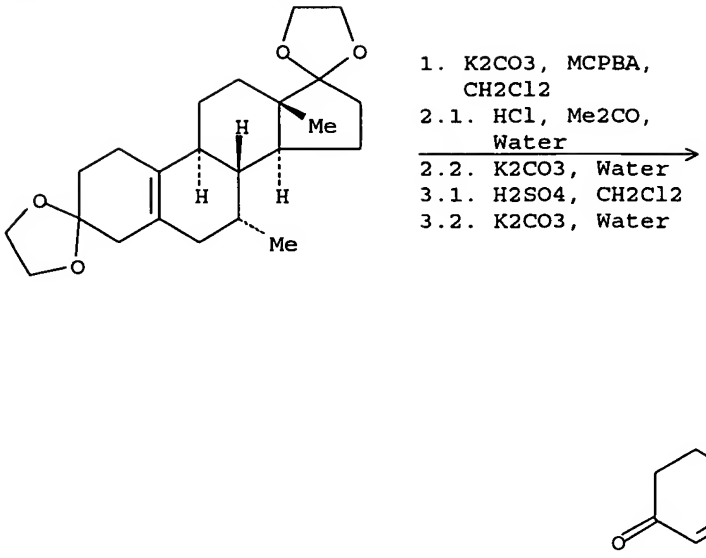


1. K2CO3, MCPBA, CH2Cl2
2. HCl, Me2CO, Water
3. K2CO3, Water
4. CH2Cl2, H2SO4
5. K2CO3, Water

(step 1)



RX(16) OF 17 - 3 STEPS



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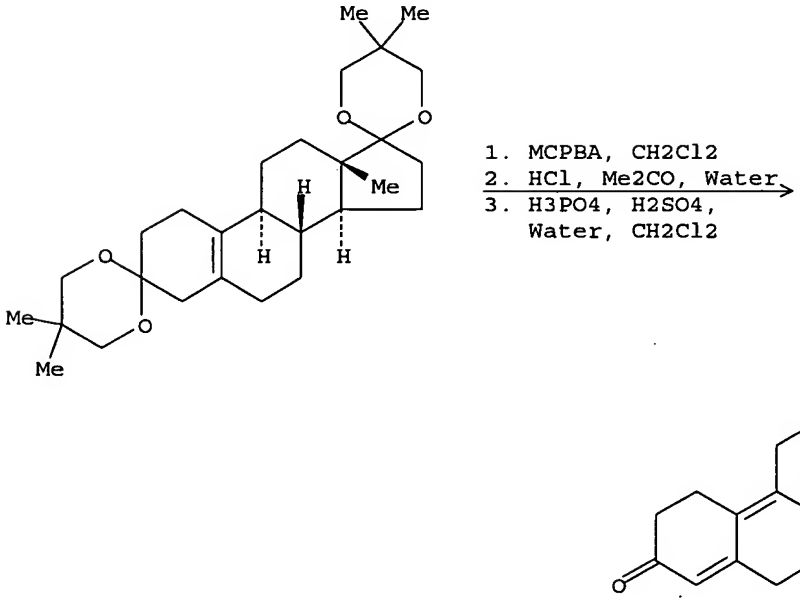

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